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NASA Aerospace Flight Battery Program


Part 1 - Volume II

Generic Safety, Handling and Qualification Guidelines for Lithium-Ion (Li-Ion) Batteries

Availability of Source Materials for Lithium-Ion (Li-Ion) Batteries

Maintaining Technical Communications Related to Aerospace Batteries (NASA Aerospace Battery Workshop)

July 10, 2008

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Appendix A. Performance Assessment

Cell Manufacturer		Sony	Yardney	Yardney	Quallion LLC				Sanyo - Distributed by Quallion in Aerospace & Military Pack Configurations (Matrix Battery Design)				QinetiQ	ABSL Spares Products Boulder, CO USA	ABSL Spares Products Boulder, CO USA	Safe	Safe	Safe	Safe	Safe	Safe	Safe
Location of Owner / Facility		Japan	Yardney	Yardney	Sylmar, CA				Japan				United Kingdom									
POC/Name, contact information		None (used in Canon BP 927 and BP 930 batteries - CFE) typically cells taken from packs. ABSL is one source for these cells.	Rob Gitzendanner, 860-599-1100.	Frank Puglia, 860-599-1100, x473	Paul Beach - 818-833-2013 - paulb@quallion.com, Vincent Visco - 818-833-2025 - vincev@quallion.com				Paul Beach - 818-833-2013 - paulb@quallion.com, Vincent Visco - 818-833-2025 - vincev@quallion.com				ABSL, Jeremy New	Tamara Max tami.max@aspace.com	Tamara Max tami.max@aspace.com	Only Space Cell	Only Space Cell	Only Space Cell	France profession nal batteries.	Only Space Cell	Only Space Cell	Only Space Cell
Cell Product Line														ABSL 18650HC	ABSL 18650HR	VES140	VES100	VES180	JPS17006	VL48E	VL44EL	VL10E
Cell P/N		18650	NCP95-1	NCP9-1	QL019KA	QL079KA	QL0032A	QL0032A	QL0032A	QL0045A	18650SA	18650W	18650V	18650F								
Cell Chemistry/Components		Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion	Li-ion
Cathode/Anode Composition	Electrolyte	LiCoO2/hard carbon Latest version with graphite	Lithiated cobalt oxide cathode with graphite anode	mixed metal oxide cathode with graphite anode	LNCAO/MCMB	LNCAO/MCMB	Mn/graphite	Mn/graphite	Mn/graphite	NMC/graphite	spinel-NMC/graphite	spinel-NMC/graphite	spinel-NMC/graphite	spinel-NMC/graphite	LiCoO2/hard carbon	Li-Ni-Mn-Co/graphite	LiNCaO/2 with graphite solvents	LiNCaO/2 with graphite solvents	LiNCaO/2 with graphite solvents	LiCoO2 with graphite solvents	LiNCaO/2 with graphite solvents	LiNCaO/2 with graphite solvents
		organic solvents with LiPF6	EC:DMC:DEC	EC:DMC:DEC:EMC	organic solvents	organic solvents	organic solvents	organic solvents	organic solvents	organic solvents	organic solvents	organic solvents	organic solvents	organic solvents	organic solvents with LiPF6							
Cell Voltage (V)																						
Avg Voltage	Max Voltage																					
	Min Voltage																					
Cell Capacity (Ahr) (at what rate?)																						
Actual	Rate for Capacity (C over)																					
Cell Mass (g)																						
Cell Dimensions																						
Cell Width or Diameter (mm)	Cell Height (mm) w/ and w/o terminals																					
	Cell Thickness (mm)																					
Cell Type (Prismatic, Cylindrical, other)																						
Specific Energy (Wh/kg) (define rated conditions)																						
Temperature for Spec Energy (deg C)																						
Discharge Current for Spec Energy (amps)																						
Energy Density (Wh/l) (define rated conditions)																						
Specific Power (w/kg) (define rated conditions)																						
Temperature for Spec Power Rating																						
Coulombic Efficiency																						
Fad Rate (% per cycle)																						
Charge Rate (C) (recommended?)																						
Discharge Rate (capability?)																						
Cell Steady State (C)																						
Cell Pulse (A)																						
Max (A)																						
Operating Temperature Range																						
Min Charge (°C)																						
Max Charge (°C)																						
Min Discharge (°C)																						
Max Discharge (°C)																						
Additional design features																						
Shut down separator																						
Non-flammable electrolyte																						
PTC																						
CID																						
Cost/Cell (\$)																						
Cell design schematics																						
Test Data																						
Characterization - charge/discharge as																						
Life (Number of Cycles)																						
DOD at quoted Number of cycles																						
Performance																						
Safety																						
Space Qualified (Y/N)																						
Thermal vacuum																						
Shock																						
Vibration																						
Flight Experience																						
Heritage - stability of source materials																						
Applications, customers																						
Recommendations																						
Limitations																						

Note: Double-click to view complete spreadsheet.

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Appendix B. Guidelines on Lithium-ion Battery Use in Space Applications

**NASA Engineering Safety Center
Battery Working Group**

**Prepared by
Barbara McKissock, Patricia Loyselle, and Elisa Vogel
NASA Glenn Research Center**

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1. Introduction

Purpose

This guideline discusses a standard approach for defining, determining, and addressing safety, handling, and qualification standards for lithium-ion (Li-Ion) batteries to help the implementation of the technology in aerospace applications. Information from a variety of other sources relating to Li-ion batteries and their aerospace uses has been collected and included in this document. The sources used are listed in the reference section at the end of this document. The Li-Ion chemistry is highly energetic due to its inherent high specific energy and its flammable electrolyte. Due to the extreme importance of appropriate design, test, and hazard control of Li-ion batteries, it is recommended that all Government and industry users and vendors of this technology for space applications, especially involving humans, use this document for appropriate guidance prior to implementing the technology.


Additional work is continuing to determine controls and testing needed for the safe use of Li-ion batteries. In addition, continuing changes in cell chemistry that affect the safe use and handling of Li-ion technology are occurring that will need to be addressed. The guidelines should be revisited and revised in one year to incorporate any newly developed recommendations.

Applications

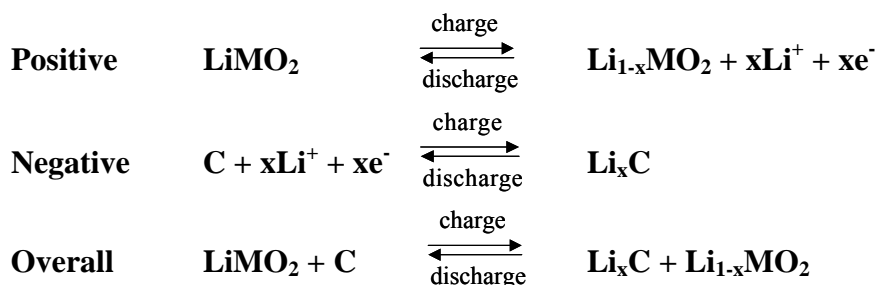
Li-ion batteries are rechargeable (secondary) batteries. Secondary batteries are used as energy-storage devices, generally connected to and charged by a prime energy source, delivering their energy to the load on demand. Secondary batteries are also used in applications where they provide power remotely from a separate power source that they return to periodically for recharge. Aerospace applications include power for satellites, astronaut suits (extravehicular activities), planetary and lunar rovers, and surface systems during night-time or peak power operations. Payloads, launch vehicles, and portable devices, such as computers and camcorders, may also use secondary batteries in place of primary batteries for cost savings, to handle power levels beyond the capability of conventional primary batteries, or because of activation, rate capability, or life issues. Li-Ion batteries were more commonly used in portable electronic equipment in the 1990s and towards the late 90s they began acceptance for powering launch and satellite systems.

2. Basic Chemical Information

There are a wide number of chemistries used in Li-Ion batteries. Li-Ion batteries avoid the reactivity, safety, and abuse sensitivity issues involved with the use of lithium metal cathodes by using a suitable alloy that allows intercalation of lithium ions; no metallic lithium is present in the cell, with normal operation. Li-Ion batteries with liquid electrolyte are rechargeable batteries and have a cathode of various classes of materials that include layered LiMO_2 ($\text{M} = \text{Co}$,


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Ni, Mn or combinations of these or other metals, i.e. Al, Mg, etc.), olivines (LiFePO₄), or spinels such as manganese oxides. The anode is usually a form of carbon, namely, coke, natural and synthetic graphites, mesophase carbon micro beads (MCMB) or carbon fibers. The electrolyte in these cells is made up of a combination of organic carbonates and a salt. The most commonly used salt is LiPF₆ (lithium hexafluorophosphate). Other salts such as LiBOB (Lithium bisoxalato borate) or LiBF₄ (lithium tetrafluoroborate) have also been used. The charge and discharge in the Li-Ion cells occurs by the process of intercalation and deintercalation of lithium ions, respectively, as shown in the equations below.




The operating voltage of Li-Ion cells varies depending on the choice of material for the anode, cathode, and electrolyte; manufacturer's recommendations for voltage limits should be followed. The capacity, life, and safety of a Li-Ion battery will also vary based on the choice of component materials. A typical Li-Ion cell will operate nominally at an average voltage of 3.6 V and the highest specific energy obtained from a state-of-the-art cell is in excess of 150 Wh/kg. The typical charging protocol for the Li-Ion cells with layered cathodes includes a constant current charge to a voltage of 3.9 V to 4.2 V (depending on the metal oxide cathode and manufacturer's recommendations) and held at constant voltage until the current falls down to approximately C/50 or C/100 (this can vary according to the manufacturer). The term, "C" signifies the charge or discharge rate, in Amperes, expressed as a multiple of the rated capacity in Ampere-hours (Ah). Due to the unique charging characteristic of the Li-Ion cells and batteries, charging requires a dedicated charger that can keep the cells and batteries within their specified voltage limits. This charger may be a "smart" charger in some cases. The discharge of the cell depends on the load used, but the end voltage during discharge should not go below 2.5 V. Typical end of discharge voltages for the batteries in different equipment has been 3.0 V/cell. Internal resistance for the Li-Ion cells varies from 9 to 120 mΩ for small (1 to 3 Ah) cells to about 0.8 mΩ for large (190 Ah) cells.

Li-Ion cells typically are spiral wound or prismatic. Under the prismatic types there are true prismatics, which are stacked flat plates, and others that are folded over to give a prismatic appearance. A third variety that is increasingly common in the market today is the elliptic cylindrical type where the spiral wound stack is flattened to give a prismatic appearance. Typically, the commercial cells used in cellular phones are prismatic cells while those used in

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camcorders, cameras, and PCs are cylindrical cells. Li-Ion cells have 100% energy efficiency through most of their cycle life (input energy is equal to output energy). Most commercial cylindrical cells are case negative, although some that have aluminum cases are case positive. Most of the prismatic cells above 5Ah capacity are case neutral. The state-of-charge (SOC) and temperature at which the cells are stored or cycled greatly affects the irreversible capacity loss in the cells. For example, one commercial cell in a period of storage for one year, exhibited less than 2 % loss at 0 % SOC and 0 °C, whereas it was about 13 % loss at 100 % SOC and 40 °C. The temperature and the depth of discharge to which the cells are cycled also affect the deliverable capacity of the cells with cycle life.

Li-Ion polymer batteries are rechargeable batteries that have polymer blends in the cathode or anode or separator or in all three. In the polymer cells, flat, bonded electrodes are used to enable the fabrication of thin cells. The cells are made in flexible shapes and sizes and packaged in aluminized plastic pouches. The electrochemical nature of these cells is very similar to the liquid li-ion cells discussed previously. These cells have a LiMO_2 cathode ($M = \text{Co, Ni, Mn}$ or combinations of these). The commonly used cathodes in li-ion polymer cells are LiMn_2O_4 spinel compounds. The anode can be any form of carbon, namely, natural and synthetic graphites, mesophase carbon micro beads (MCMB) or carbon fibers (li-ion polymer cells). The anode can also be lithium metal (lithium polymer cells). The electrolyte in these cells is made up of a combination of organic carbonates and a salt in a polymer matrix. The most commonly used salt is LiPF_6 (lithium hexafluorophosphate). The polymers commonly used are based on polyacrylonitriles (PANs), PVDF based polymers (PVDF-HFP, PVDF-CTFE), polyvinyl chloride (PVC), etc. In some cases, an ancillary plasticizer such as dibutyl phthalate is incorporated into the resin, which facilitates the densification of the electrodes under low temperature and pressure. The plasticizer is later vaporized or removed by a suitable solvent extraction process. The nominal voltage of the Li-Ion polymer cells with the cobaltate cathode is about 3.6 V and the energy density obtained can range from 145 to 190 Wh/kg. The Li-Ion polymer cells with the manganese spinel cathode have a nominal voltage of about 3.8 V and have energy densities in the range of 130 to 144 Wh/kg. The typical charging protocol for the lithium/Li-Ion polymer cells includes a constant current charge to a voltage of 4.1 V or 4.2 V (depending on the metal oxide cathode and manufacturer's recommendations) and held at constant voltage until the current falls to approximately C/100 (this can vary according to the manufacturer). Similarly to the li-ion cells with liquid electrolyte, charging of li-ion polymer cells requires a dedicated charger due to their unique charging characteristics. This charger can be a "smart" charger in some cases. The discharge of the cell depends on the load used but the end voltage during discharge should not go below 2.5 V. Typical end-of-discharge voltages for the batteries in different equipment have been 3.0 V/cell. Internal resistance for the li-ion polymer cells varies from 20 to 60 mΩ for small (0.5 to 15 Ah) cells and is expected to drop with increased capacity cells.

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Advances in cathode and anode materials have led to the development of new Li-Ion cell chemistries. Such changes also cause a change in voltage. The Olivine cathode is one such with its LiFePO_4 cathode. The operating voltage of the LiFePO_4 type li-ion cell is 3.3 V. Changing anode materials from graphite to titanate-based materials as in the Altairnano cells is another example where the operating voltage drops to 2.65 V.

Li-Ion polymer cells are typically flat and thin. The cells are packaged in vapor-impermeable, flexible, multilayer polymer-aluminum bags. The polymer cells are typically made up of a positive electrode plate and a negative electrode plate bonded to two opposite sides of an ionically conductive separator. The plates can be stacked as individual plates, Z-folded, or folded in other ways depending on the mechanical properties of the individual component layers. A large capacity cell would thus have several plates stacked on each other to give the capacity required. Another common method of cell stacking is the “bicell” configuration where the central plate (typically a negative electrode) is shared by two positive plates on either side. There is a layer of separator between the center negative plate and the two positive plates on either side. Several bicells can be stacked to give a larger capacity cell. Polymer cells typically perform well at low rates of charge and discharge. However, cells can be made for specific medium and high rate applications. Because of the higher resistance caused by the polymer materials used in the electrodes and separator, currently, a small quantity of liquid electrolyte is used to improve ionic conductivity. The state-of-charge (SOC) and temperature at which the cells are stored or cycled greatly affects the irreversible capacity loss in the cells. These are similar to the liquid li-ion cells.


3. Factors affecting battery performance

The performance required from the battery for a specific application should be determined and the relative importance of the different factors should be prioritized prior to selection of the cell to be used, since they interact with each other. For example, operational factors such as temperature and charge/discharge rate affect other factors such as capacity, voltage, and life. Typically, testing is required to confirm battery performance at the specific conditions of the application. General interactions of these factors are discussed here; information on the performance of specific cells at defined conditions can be requested from manufacturers.

Capacity

Capacity is adversely affected by high storage temperatures, high state-of-charge during storage, higher discharge rates, low temperature during charging, the stand time between charge and discharge, and operation at temperatures either lower or higher than the cell optimum temperature.

Voltage

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When a cell is discharged, its voltage while under load is lower than both the theoretical voltage, which is based on its chemical composition, and the open-circuit voltage, where there is no load on the cell. The voltage of the cell decreases during the discharge, and the shape of the discharge voltage curve is affected by temperature, discharge rate, cycle life, service life, and the electrochemical reactions occurring within the cell. The voltage typically is lower and decreases faster with increased discharge rates and longer cycle life. The open-circuit voltage varies with the state-of-charge of the cell.

Discharge Current Rate

Decreased capacity, voltage, and life and increased IR losses and heating are seen with higher discharge current rates, along with a more rapid decrease in voltage during the discharge. A cell that has been discharged at a higher current rate to a specific cutoff voltage still has additional capacity available above that cutoff voltage if the discharge is continued at a lower current rate. While the theoretical voltage and capacity can be approached with extremely low current rates, very long discharge periods can cause chemical deterioration that would reduce the capacity. Discharge rates are commonly specified as multiples of the C rate, which is the current that will discharge the battery to the cutoff voltage in one hour.

Charge Current Rate


Less capacity is restored and increased heating occurs when higher charge current rates are used. The magnitudes of the capacity decrease and heating increase are temperature dependent. When a cell is charged at a higher current rate to the end-of-charge voltage, more capacity can be added below the cutoff voltage if the charge is continued at a lower rate. Charge rates are also commonly specified as multiples of the C rate.

Continuous or Intermittent Discharge

When a battery is allowed to rest after a discharge, certain chemical and physical changes take place that can result in voltage recovery. Thus, the voltage of a battery that has dropped during a high-rate discharge will rise after a rest period. This improvement due to the rest period is generally greater after discharge at higher currents and also is dependent on the end-of-discharge voltage, temperature, and the length of the rest period.

Constant Current, Constant Load, or Constant Power Discharge

A battery may be discharged using constant current, constant resistance, or constant power loads, or variable loads depending on the requirement of the application. The discharge current varies for each type of discharge. The time that the battery will deliver the required capacity is inversely proportional to the average current. In the constant-resistance discharge mode, the discharge current decreases as the battery voltage drops and the power decreases as the square of the battery voltage. Under this mode of discharge, to assure that the required power is available at the end-of-discharge voltage, the current and power during the earlier part of the discharge start higher than the minimum required. The battery discharges at a high current, draining its

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ampere-hour capacity rapidly and excessively, which will result in a shorter discharge time. In the constant-current mode, the current is set so that the power output at the end-of-discharge voltage is equal to the minimum level required. Thus, both current and power throughout the discharge are lower than for the constant-resistance mode. The average current drain on the battery is lower and the discharge time is longer. In the constant-power mode, the current is lowest at the beginning of the discharge and increases as the battery voltage drops in order to maintain a constant-power output at the level required by the equipment. The average current is lowest under this mode of discharge, and hence, the longest discharge time is obtained.

Temperature


The temperature at which the battery is charged and discharged has a pronounced effect on its capacity and voltage characteristics. This is due to the reduction in chemical activity and the increase in battery internal resistance at lower temperatures. Lowering of the discharge temperature will result in a reduction of capacity, as well as an increase in the slope of the discharge curve. The optimum temperature is dependent on the specific battery chemistry and design and can be tailored somewhat. For most Li-ion batteries the optimum temperature is between 20 and 40°C, although electrolytes have been developed by JPL for their rover missions that allow good performance at lower temperatures. At higher temperatures, chemical deterioration may be rapid enough during the discharge to cause a loss of capacity, the extent again being dependent on the battery system and temperature. As the discharge rate is increased, the cell voltage decreases; the rate of voltage decrease is usually more rapid at lower temperatures. Similarly, the cell's capacity falls off most rapidly with increasing discharge load and decreasing temperature. Discharging at high rates could cause anomalous effects as the battery may heat up to temperatures far above ambient, and thus show the same effects of operating at higher temperatures. Some chemistries exhibit voltage delay when discharging at high rates and low temperatures, where the voltage starts low and slowly increases over the first several minutes of discharge. Voltage delay becomes more pronounced as temperatures decrease and rates increase.

Service Life

The most accurate method of determining service life is to run an actual life test of the battery at the operational conditions and run the battery until it can no longer provide the required energy, which is defined as the end of life. There are also various mathematical calculations that can be used to approximate the performance of a given cell or battery under a particular discharge condition and/or to estimate the weight or size of a cell required to meet a given service requirement.

Voltage Regulation

The voltage regulation required by the equipment restricts the capacity obtainable from a battery. Allowing the lowest possible end-of-discharge voltage and the widest voltage range leads to the highest available capacity. Discharging multi-cell series-connected batteries must be controlled

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to prevent safety problems that might arise from mismatched or unbalanced cells. When operated in a series string, the voltage must be controlled to prevent the lowest voltage cell from being driven into voltage reversal possibly resulting in cell venting or rupture.

A voltage regulator can be used to convert the varying output voltage of the battery into a constant output voltage consistent with the equipment requirements. This allows the full capacity of the battery to be used; the only tradeoff is that the voltage regulator has losses.

Another consideration is the response of the cell or battery voltage when the discharge current is being changed during the discharge. A battery with lower internal resistance will have a smaller drop in voltage and better response to changes in load current than one with higher internal resistance.


Charging Voltage

The specific voltage and the voltage profile on charge depend on such factors as battery chemistry, charge rate, temperature, life and electrochemical changes that may have occurred in the cell due to aging. Charge control is required for li-ion batteries to prevent overcharge, which can cause venting or rupture. The manufacturers' recommendations for maximum voltage should be followed and care should be taken to ensure that the recommendations are applied at the cell level.


Storage Conditions and Calendar Life

Batteries are a perishable product and deteriorate as a result of the chemical action that occurs during storage that results in self-discharge. The type of cell design, chemistry, temperature, state-of-charge, and length of storage period are factors that affect the shelf life or charge retention of the battery. The type of discharge following the storage period will also influence the shelf life of the battery. Usually the percentage charge retention following storage (comparing performance after and before storage) will be lower for more stringent discharge conditions. Since self-discharge proceeds at a lower rate at reduced temperatures, refrigerated or low-temperature storage extends the shelf life and is recommended for some battery systems. Refrigerated batteries should be warmed to the optimum operational temperature suggested by the manufacturer before discharge to obtain maximum capacity and to avoid condensation. Li-ion batteries should be stored at lower states-of-charge to avoid chemical changes in the battery which cause decreased battery performance. Follow the manufacturer's guidelines for optimum storage conditions. The self-discharge characteristics of a cell that has been or is being discharged can be different from those of a cell that has been stored without having been discharged. Knowledge of the battery's storage and discharge history is needed to predict the battery's performance under these conditions. This information is usually available from the battery manufacturer or storage facility.

Cycle Life

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The number of charge/discharge cycles that have been performed by the battery affects both the voltage and capacity of the battery. As a battery is cycled, lower voltages and less capacity are available on discharge. These impacts are greater at more severe discharge conditions.

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Vibration and Shock

Vibration and shock can cause internal shorts that can lead to venting of the electrolyte, possible fire, and thermal runaway. It can also lead to fracture of the cell case, which can lead to electrolyte leakage. The ability of the battery design to withstand the anticipated vibration and shock conditions should be evaluated by testing prior to use.

Other Environments


Other environments encountered by the battery during its life could impact its eventual performance. These could include humidity, fog, fungus, fine sand, explosive atmospheres, and radiation. The impacts of the various environments experienced by the battery over its life should be evaluated on a case-by-case basis.

4. Battery Design

The design of a multi-cell battery should ensure electrical continuity, mechanical stability, and adequate thermal management. The battery must provide both the capacity and current required within the voltage limits of the application. The performance of the cells in a multi-cell battery will usually be different than the performance of the individual cells. The cells cannot be manufactured identically and each will encounter a somewhat different environment in the battery pack. The design of the multi-cell battery (such as packaging techniques, container material, insulation, and potting compounds) will influence the performance as it affects the environment and temperature of the individual cells. Obviously these battery materials add to the size and weight and the specific energy or energy densities of the batteries will be lower than that of the component cells. A Failure Modes and Effects Analysis (FMEA) should be done for all battery designs. All cell safety devices (such as vent disks, current interrupt devices, positive temperature coefficient devices, fuses, and switches, relays, and diodes) incorporated into the battery design must have their failure modes and reliabilities included in the overall battery failure and reliability analysis, since they increase the number of failure scenarios.

Whenever a choice exists between different risk-levels associated with chemistry, capacity, complexity, charging and application, the option that presents the minimum risk while meeting the performance requirements of the mission should be selected. For example, battery selection for in-cabin applications must not be justified only on a cost and schedule basis of commonality with similar or identical EVA or payload application batteries. For aerospace applications, the hazard severity of the battery is evaluated as part of the battery design evaluation and approval.

Battery electrical design should minimize the risk of leakage currents from the cell terminals to the battery case and electrostatic discharge and should meet all EMI and compatibility requirements for the application. Battery charge control is required for li-ion batteries to avoid the hazards associated with overcharge and should be developed along with battery design. With

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rechargeable li-ion batteries, cycling could cause the cells in a multi-cell battery pack to become unbalanced and their voltage, capacity, or other characteristics could become significantly different. This could result in poor performance or safety problems. The amount of acceptable cell state-of-charge divergence depends on the battery application. Applications with large capacity margins may be able to charge and discharge to the weakest cell limits without requiring cell-level control. For applications with long cycle life requirements or little capacity margin, it is more likely that cell-level monitoring and end-of-charge or discharge control will be required for reliable battery performance and safety.

Batteries and battery containers must be designed to survive all environmental conditions of a mission or application. This includes launch/abort/landing loads, transportation, and handling environments. Mounting or sealing of cells in a battery case should not interfere with cells vents or rupture disks.


Battery designs that retain the heat dissipated by the cells can improve performance at low temperatures. On the other hand, excessive buildup of heat can be injurious to the battery's performance, life, and safety. The battery thermal design needs to maintain an optimal temperature range for all the cells in the battery within the expected environmental conditions.

Vendors of cells used in aerospace battery designs should have a formal quality control plan in place prior to cell production.

5. Hazards and Controls

The main abuse conditions that cause hazards conditions in li-ion cells are the result of overcharge, external and internal short circuits, overdischarge, high temperatures, and structural issues.


Studies have shown that overcharge conditions can lead to the deposition of lithium metal that can create internal shorts in the cell and breakdown of electrolyte that can lead to increased internal pressure. The electrolyte in the Li-Ion cells contains flammable organic solvents and under high voltage conditions, they decompose leading to the formation of gases (carbon monoxide, carbon dioxide, and other gaseous decomposition products). This can cause over-pressure conditions inside the cell leading to smoke and flame if the gases are not vented benignly. Another major hazard that exists with certain transition metal oxide cathodes is the evolution of oxygen under overvoltage conditions. This occurs due to the instability of the transition metal oxide structure at high voltages that causes the release of oxygen. The presence of oxygen and the flammable gases at high voltages cause excessive gas pressure inside the cells that can result in venting with flames. Li-Ion cells must not be charged to a voltage greater than that recommended by the vendor. Li-Ion batteries require a dedicated charger or a universal

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“smart” charger that recognizes the battery chemistry. The charging scenario and charging equipment should be evaluated as part of the battery design evaluation and approval process. Final testing should treat the battery and charger as a unit or system. Many Li-Ion cells have built-in current interruption devices (CIDs) that help protect the cell from overcharge.

Short circuits are a direct connection between the positive and negative terminals of a cell and/or battery. They can be generated by a failure external to a cell or by a failure internal to a cell. External short circuits can be caused by faulty connections between the positive and negative terminals of a cell and/or battery, conductive electrolyte leakage paths within a battery, broken and/or loose connections within a battery, or structural failures, loads experienced by the battery, or failures in the hardware powered by the battery. External shorts of Li-Ion cells can result in very high current spikes that cause high pressures inside the cell resulting in venting and explosions. External shorts are prevented by a variety of methods. Many li-ion cells have built-in current interruption devices (CIDs) that trip due to internal pressure at currents well below the battery's short circuit current capability, which prevent further discharge through the external short and save the battery if short circuits occur. If this capability is not built into the cell, it needs to be addressed at the battery level. Interrupters may be fuses, circuit breakers, thermal switches or other effective devices. Some cells also have positive temperature coefficient (PTC) devices that are used to limit the high current spikes experienced by a cell/ battery under an external short condition. However, when used in series strings or parallel/series designs, they may not give the same protection as seen in independent cells. Both PTCs and CIDs may fail when exposed to high voltages due to other failures. The use of bypass diodes is recommended to prevent these failures. The maximum number of cells in series without a bypass diode depends on the cell being used and is determined by testing. To prevent shorts between leaked electrolyte and the battery case, all inner surfaces of metal battery cases should either have an anodized finish or be coated with a non-electrically conductive, electrolyte-resistant paint. Cell terminals need to be protected from contact with other conductive surfaces. The surfaces of battery terminals on the outside of the battery case also need protection from accidental bridging. Battery terminals which pass through metal battery cases should be insulated from the case by an insulating collar or other effective means. The surfaces of battery terminals that extend inside the battery case need to be insulated with potting materials to prevent unintentional contact with other conductors inside the case and also to prevent bridging by electrolyte leaks. Wires inside the battery case should be insulated, restrained from contact with cell terminals, protected against chafing and physically constrained from movement due to vibration or bumping. Internal shorts are caused by metallic burrs, misalignment, separator failure, or other means of direct contact between the positive and negative materials inside a battery cell. Testing the ability of the battery box and connections to handle a 500 V difference without current leakage is recommended to detect latent shorts in the battery circuitry.

Li-Ion cells under simulated internal short conditions can exhibit venting, fire, smoke, and go into thermal runaway. Slight deformations of the cells under hydraulic jaw pressures of 20 to 50


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psi per minute, causing soft shorts, have resulted in electrolyte leakage and smaller rises in temperature (max. temp. 45°C recorded). Fast and heavy crushing (hydraulic jaw pressures of greater than 200 psi per minute) of the cells has resulted in venting and smoke. Internal shorts must be prevented with quality-controlled assembly procedures, wherever possible; however, the incorporation of external cell and battery-level short circuit protection devices can stop the propagation of other hazards should a rare internal short occur. Batteries for manned applications are screened for tolerance to internal shorts using the vibration screening method discussed below in section 8.

From a battery perspective, high temperature occurs when the operating temperature of a battery or cell exceeds the upper temperature limit of the manufacturer's performance specifications. Li-Ion cells subjected to very high temperature conditions (about 130-190°C depending on chemistry) can vent, smoke, and exhibit thermal runaway accompanied by fire and/or an expulsion of can contents through the vent holes in the cell. An additional high temperature concern for batteries and cells is the maximum safe touch temperature if they will be handled by crew. Internal causes of high temperature leading to thermal runaway can be controlled by controlling shorts; by the incorporation of PTCs, which interrupt the current before a hazardous temperature is reached; by inclusion of a shutdown separator, which causes a meltdown of the middle layer of a three-layer separator at high temperatures and interrupts the electrochemical reactions in the cell; and by operating the cell within the load limits established by the manufacturer. Heat sinks, heat shunts, and active cooling loops can also be used to remove excess heat from internal or external sources. Thermal analysis or testing of the battery in expected surroundings should be performed to verify battery temperatures throughout anticipated operational conditions.

Overdischarge conditions lead to the electrodeposition of copper on the cathode causing the formation of a short circuit condition when the cell is subsequently charged. In most cases, overdischarge is benign and results in a dead cell. Voltage dispersion between cells in a string can occur over the operational life of the battery. In a string configuration, the presence of a weak cell can cause an imbalance in voltage and also lead to an overdischarged cell. During subsequent string charging with no cell-level voltage or mid-string monitoring or control, the unbalanced cells could result in overcharging of some cells especially if the weak cell has a soft short due to its overdischarged state.

Structural hazards can result from mechanical, chemical, and thermal stresses that reduce the integrity or functional capability of cell and battery cases. These can lead to breakage of cases, seals, mounting provisions, and internal components, which can lead to internal shorts and unconstrained movement of the battery. Battery designs are tested for vibration and shock appropriate for the expected environment. Materials used in battery designs should not degrade if exposed as expected to each other. Effects of possible thermal expansion should be accounted for.

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The main abuse conditions that cause hazardous conditions in li/li-ion polymer cells are the result of overcharge, internal and external shorts and high temperatures. These are very similar to that for the liquid li-ion cells discussed above. However, the polymer li-ion cells have an additional problem with electrolyte leakage under abusive conditions. Electrolyte leakage can lead to short circuits, corrosion, and chemical exposure. The main control for electrolyte leakage is to control abuse conditions as listed above.

6. Battery Requirements

CREWED SPACECRAFT

This section is geared toward the designers of batteries to be used in crew equipment or crewed vehicle systems and payloads. All batteries are designed or battery designs chosen to control applicable hazards and these designs must be reviewed prior to certification for flight. Specific design and verification requirements for a battery are dependent upon the battery chemistry, capacity, complexity, charging and application. There are basic requirements of all battery designs and applications that should be followed. These mandatory requirements are listed in this section.

Battery Requirements Summary

The following is a summary of battery requirements for crewed missions according to NASA Johnson Space Center. Refer to the Payload Safety Review Panel (PSRP) website at <http://wwwsrqa.jsc.nasa.gov/pce/default.htm> for the latest requirements. Specific design and verification requirements for a battery are dependent upon the battery chemistry, capacity, complexity, charging and application. There are basic requirements of all battery designs and applications that must be followed.

Battery Design Evaluation and Approval

Every battery, its verification-screening program, its on-orbit usage plans, and its post-flight processing are evaluated and approved by the battery engineers of the applicable Power Systems Office or by the Payload Safety Review Panel prior to certification for flight of that battery as early as possible during the design phase of a battery or battery-powered application. Past experience has shown that if a battery evaluation does not occur until the design is nearly complete (or completed); changes in the design have often been required. Approval of a battery design for a particular hardware will not be construed as a general certification. Approval of battery usage needs to be obtained for each hardware configuration. The process for obtaining battery design evaluation and approval from JSC is detailed in EA-CWI-033. Ideally, the battery design and its screening program will be completed and approved at the completion of the critical design review or equivalent phase of a project. The following items should be addressed:

- the battery hazard controls are adequately addressed per JSC-20793 guidelines

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- the cell screening or battery-pack screening plan is adequate per JSC-20793 guidelines
- the plans for on-orbit usage and provisions for on-orbit disposal or return of unused cells or battery packs are adequate
- the post-flight processing plan for battery removal and disposal is adequate

Payload Battery Approval

Payload battery approval is only one part of the overall payload safety approval process. Payload providers for the ISS should follow the "Payload Safety Review and Data Submittal Requirements," NSTS/ISS 13830, to submit a payload for review. A Flight Payload Standardized Hazard Control Report, JSC Form 1230, will be submitted to document all hazards for the payload, including the battery-related hazards. Unique hazard reports may be required if the batteries chosen do not meet the requirements stated on the JSC Form 1230 summarized below. Further guidelines for payloads are found in the "Safety Policy and Requirements for Payloads Using the Space Transportation System," NSTS 1700.7, and "Safety Policy and Requirements for Payloads Using the International Space Station," NSTA 1700.7 Addendum. All payload batteries that utilize series and parallel combinations need a unique hazard report and all payload cells need to pass specified acceptance-screening tests.

Overview of the Payload Safety Review Process

The Payload Organization (PO) will ultimately be responsible for providing the proper test data and manufacturers information/certification which supports the choice of a particular battery chemistry according to current versions of NSTS/ISS 1700.7, NSTS/ISS 1700.7 ISS Addendum, and NSTS/ISS 13830. Prior to battery selection, the PO should contact the Payload Safety Review Panel and request information on prior flights of candidate battery chemistries used in payloads with similar energy storage requirements. If the batteries being considered have a prior safety history, less testing may be required, or the limits of required testing may be adjusted according to known weaknesses. The PSRP determines the type and quantity of data to be supplied. The PSRP will also recommend suitable batteries if requested by the PO. The PO may also request that a JSC battery engineer conduct the various screening tests required to ascertain battery safety status. This is subject to the availability of the JSC battery engineer, appropriate testing facilities, and project funding. The PO may also request a safety Technical Interchange Meeting (TIM) prior to a formal Phase 0/1 Safety Review, to discuss the payload energy storage requirements, and which battery chemistries are being considered. The PO should be prepared to discuss their battery test program, qualification philosophy, proposed packaging of the batteries, and series/parallel configuration if more than one battery string is being considered. The PSRP may assign a JSC battery engineer, a JSC payload safety engineer, or battery specialist to consult with the PO. The PSRP reserves the right to request additional data or testing depending on the battery selection. The battery safety approval process for all payloads is dictated by the PSRP or its duly designated representative. This process should be entered into as early in the payload design process as possible (once energy requirements have been determined), so that the PSRP and the PO can agree upon a process specific to the potential battery chemistry and the specific

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power needs of the payload. An acceptable battery design includes controls for potential battery hazards. Battery design considerations must be given to the structural integrity of the cell and battery housings, the possibility of gas generation, pressure, and/or electrolyte leakage, the prevention of short circuits and circulating currents, the possibility for high battery temperatures, over-discharging; and assurance of proper charging techniques. The designer should refer to the details given in this document regarding each hazard, its sources, and its controls. The battery evaluation will assess the battery hazard controls. Depending on the battery chemistry, capacity, complexity, charging and application, certain hazard controls discussed previously may be imposed upon the specific battery as unique design requirements.

Fault Tolerance

The fault tolerance of the battery will be evaluated as part of the battery design evaluation and approval. For the purposes of fault tolerance discussions, NPR 8705.2 defines “catastrophic hazard” as a hazard that can result in the potential for: a disabling or fatal personnel injury or loss of the space vehicle and ground facilities or loss of vehicle. Permissible non-catastrophic failure modes for various batteries have been identified and can be properly controlled by the battery design. To summarize, NPR 8705.2 requires that all batteries will be two-fault tolerant to catastrophic failure. The two-fault tolerance requirement, where a battery survives any two credible failure modes without inducing any catastrophic hazards and any single failure without inducing critical hazards, is also a sound engineering approach to crewed space flight battery applications. Historically, this requirement is derived from NSTS 1700.7 and its corresponding ISS Addendum. These documents reinforce the two-fault tolerance requirement as a sound engineering approach to manned space flight battery applications. Within this requirement, permissible failure levels for batteries have been established and must be incorporated in the battery design requirements. The hazard reduction precedence will be evaluated as part of the battery design evaluation, approval and Battery Office certification. Batteries and their systems must be inherently safe through the selection of appropriate design features or the use of appropriate safety devices, as fail operational/fail safe combinations to eliminate the hazard potential.

Since lithium-based cells/batteries have a high specific energy and hazard potential, they are required to be at least two-fault tolerant to any catastrophic failure unless a more stringent requirement is dictated by the previous sections. Most lithium based cell electrolytes present corrosive, toxic, or flammability hazards. With appropriate lot-verification testing, tolerance of lithium cells to certain types of abuse may count as a hazard control, dependant on cell design, capacity, complexity, charging and application. A cell failure is counted as one of the failures.

Critical Equipment

Critical equipment includes equipment whose functional failure can result in loss of the vehicle, harm to personnel, or inability to achieve primary mission operational objectives. The permissible failure levels are defined in terms of one and two successive failure modes.

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- A. A critical equipment battery must survive any single credible failure mode without causing damage to equipment.
- B. A critical equipment battery must survive any single credible failure mode without requiring contingency procedures.
- C. A critical equipment battery must survive any single credible failure mode without requiring emergency procedures.
- D. A critical equipment battery must survive a subsequent second failure without causing personnel injury.
- E. A critical equipment battery must survive a subsequent second failure without causing loss of vehicle.
- F. A critical equipment battery must survive a subsequent second failure without causing loss of ground facilities.

GFE/ CFE/Payload/Crew Equipment Batteries (Non-Critical)


Most non-critical equipment include calculators, cameras, multimeters, tape recorders, and others are already certified for flight and are listed for waivers to detailed testing. These are of the button cell type in most cases.

Although there are virtually no requirements specific to batteries, the permissible failure level is classified as a "soft" failure. That is, any failure is permissible, so long as no credible failure can propagate outside the equipment or to a piece of critical equipment. Analysis of this non-propagation should be documented and appended to the appropriate safety data package.

Hazard Controls

A battery design includes controls for potential battery hazards. Battery design considerations must be given to the structural integrity of the cell and battery housings; the possibility of gas generation, pressure, and/or electrolyte leakage; the prevention of short circuits and circulating currents; the possibility for high battery temperatures; over-discharging; and assurance of proper charging techniques. The battery evaluation will assess the battery hazard controls.

Li-Ion batteries must be charged with a dedicated charger or a universal "smart" charger that recognizes the battery chemistry. The charger should be evaluated under normal operating conditions to understand its characteristics and verify its safety. The batteries must undergo engineering evaluation to discern the characteristics of the system. The battery must be two-failure tolerant and hence should have at least two levels of safety for any given hazardous condition. The batteries should have protection against overcharge and overdischarge conditions and protection against over-current (fuse) and/or over-temperature (thermal fuse). Commercial cylindrical 18650 cells have three levels of protection. These are the PTC (Positive Temperature Coefficient), CID (Current Interrupt Device), and the shutdown separator. The PTC is activated in the case of external short/over-current and over-temperature conditions. The CID is activated when the cells build up excessive pressure that usually occurs when the cells are overcharged to

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voltages close to or above 5V. The shutdown separator is activated when the cells reach a certain temperature that causes a meltdown of the middle polyethylene-layer of the three-layer separator. This usually occurs at about 130°C. The cells also have a vent that is rated to vent above 150 psi but this is not a level of protection as the cells go into a thermal runaway condition with venting. Large cells consist of the shut-down separator, vents, and a fusible link to the electrode as levels of protection. The shut-down separator is activated when the cells reach temperatures of close to 130°C. The fusible link melts at specific currents, which then inhibits any hazardous occurrences during an external short condition. The vent typically operates above 150 psi and the vent can sometimes be a level of protection to a catastrophic hazard but the cells typically do not perform after venting.

For Li-Ion batteries of the COTS type with up to 10 V and up to 60 Wh, data should be provided to show one-fault tolerance. The second level of control should be obtained from existing test data or manufacturer's data. Batteries and charger should be acquired from the same lot and the battery safety circuitry and charger circuitry information should be provided. All flight batteries undergo acceptance testing that includes visual inspection and testing for open circuit voltage, closed circuit voltage, vibration to flight requirement levels or higher (see section on short circuit hazards) and vacuum leak check with functional charge/discharge cycles performed before and after each test.

Engineering and qualification of Li-Ion batteries and cells, lot certification, acceptance testing and screening of flight batteries is performed on all batteries that are not already approved, and the EP-WI-015 can be used as the guiding document. Lot testing should be performed on at least 3% cells of every new lot of cells and batteries procured for the same application.

The Li-Ion batteries should undergo performance and abuse tests on the battery and cell level to establish an engineering evaluation database. The performance tests must include physical characterization (dimensions and weight), electrochemical characterization (OCV, CCV, capacity checks), rate capability (capacities at different charge/discharge rates and different temperatures), and vacuum leak checks. The abuse tests must consist of overcharge, overdischarge, external short, internal short/crush, heat-to-vent, vibration, drop, and vent and burst pressure determination. The main features that need to be understood about the battery are the fuse rating, the operational characteristics (voltage) of the overcharge and overdischarge protection switches and the nature of the protective circuitry. On the cell-level, the levels of safety incorporated into the cell, if any, need to be understood and characterized (for example, PTCs, CIDs, shut-down separator, etc.).

The qualification of the battery should include testing the batteries to environmental and vibration levels that are higher than the mission requirements. (See the discussion on Short Circuit Hazards). The flight acceptance testing involves verification of battery performance by charge/discharge cycling, vacuum leak checks and vibration. The number of flight missions that

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the batteries will be used for, along with the location of the battery in the Orbiter should determine the period and level of vibration. The vibration spectrum used to screen the batteries from the occurrence of internal shorts should be higher than what is obtained from the calculation of mission requirements. Thermal analysis should be done for the expected load/charge profile.

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Crew Touch temperature requirements

Hardware which will be touched by crewmembers must have surface temperatures not exceeding 45 °C for continuous contact, should have warning labels for surface temperatures between 45 and 50 °C and should have protective measures above 50 °C. If a battery or cell will be touched by a crewmember, the battery must incorporate additional protection to prevent the battery and/or cell temperature from exceeding this 45°C limit. If the battery or cell will not be directly touched but is located near a surface that will be touched, temperature controls must be incorporated to prevent excessive battery or cell heat from transferring to the touchable surface.

Flight Cell and Battery Pack Qualification, Lot and Flight Acceptance Testing

Qualification, lot and flight acceptance tests are used to verify the effectiveness of redundant hazard controls for catastrophic failures. The overall flight cell and battery pack testing requirements follow.

- A. The hardware provider performs qualification testing as defined per the approved qualification and acceptance test plan for the hardware project.
- B. The hardware provider performs acceptance tests on loose cells and/or battery packs before the cells and packs are installed in the battery-powered flight hardware.
- C. The hardware provider performs lot testing as defined per the approved lot test plan for any new lot of batteries purchased for the hardware project.
- D. The applicable NASA Power Systems Office approves all proposed acceptance and qualification test procedures.
- E. Test plans include analysis and/or verification of battery safety circuitry.

Detailed requirements for acceptance testing and qualification testing are given in the following subsections. Details of the overall battery process are provided in EA-CWI-033.

Flight Cell and Pack Verification Acceptance Testing

Acceptance tests are performed on loose cells and battery packs before the cells and packs are installed in the battery-powered flight hardware. The proposed acceptance-test procedure is approved by the PSRP as part of the battery evaluation. Acceptance testing for Li-ion and Li-polymer cells and batteries include visual inspection, vacuum/leak check, dimensions and weight measurement, open circuit voltage and closed circuit voltage checks, cycle testing, vibration, and thermal cycling. The cell and battery pack acceptance test plan will be evaluated as part of the battery design evaluation and approval. Offgassing/out-gassing tests may be required for materials compatibility. Any cell displaying any evidence of electrolyte leakage fails these screening tests. Data from the cell and battery pack screening should be recorded and included as part of the hardware data package. Users should verify that all cells and batteries intended for flight use are within the designated shelf life based on the cell manufacture date as specified in the Limited Life Items database which is located at <http://wwwsrqa.jsc.nasa.gov/gfe/CDS/qryCDS.asp>. Button cells of 300 mAh capacity or less that have a solder joint to a circuit board or component are exempt from cell acceptance test requirements; however, UL test data are needed for the specific coin cell and a visual check for

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leakage and a functional test of the hardware s required. Acceptance tests are also be carried out on all battery circuit components used in the assembly of a multicell battery. This includes diodes, smart chips, resistors, thermistors, polyswitches, thermostats, mechanical and solid-state switches, and fuses. Fuses need to be checked for continuity. After completion of the cell and battery pack acceptance testing, the flight cells or batteries are installed in the hardware and the equipment tested and prepared for flight per the hardware provider’s requirements. Alternatively, the user may decide to store cells/batteries separately from the hardware to avoid inadvertent or parasitic power depletion. The hardware should be maintained at ambient or chilled storage conditions from the time of bag and tag until flight as specified by the battery manufacturer/hardware provider.

Flight Cell and Battery Pack Qualification Testing

The qualification testing is conducted at the cell level and battery-level (i.e. on the stand-alone battery) as well as at the integrated, top-level assembly (i.e. with the cells or battery pack installed in the top-level assembly). Determination of the qualification and certification test plan is achieved via inputs from the battery evaluation process, the intended application, and the program (i.e. Shuttle or Station) requirements. Typical testing includes functional checkout (operational, cycle), environmental (i.e. vibration, thermal, thermal vacuum), electromagnetic compatibility, power quality, or others as deemed appropriate for the specific hardware and application. The vibration spectrum varies depending on the cell chemistry and tolerance of the cell to internal shorts. The information for vibration testing is provided the section on short circuit hazards below. The safety tests that are required to prove two-fault tolerance to catastrophic hazard are performed as part of a qualification test program and repeated for each newly purchased lot of the same battery. The flight cell and battery packs that form the flight lot can go into the flight acceptance testing after the qualification test has been successfully completed.


Planetary Protection and Cleanliness

For planetary and lunar missions, general cleanliness and contamination control requirements need to be addressed during the manufacturing and assembly of flight batteries. In addition, as a part of planetary or lunar spacecraft, the battery is subject to NASA Planetary Protection requirements, and special precautions will be taken during final assembly to limit the numbers of trapped microbes in the assembly.

UNMANNED SPACECRAFT

Acceptance and Qualification Testing

Acceptance testing will include cell and battery capacity tests at several temperatures and C-rates, battery charge retention tests, battery impedance, and battery isolation tests. For qualification, the batteries and cells must meet the voltage requirements at the current during testing without variation in operating levels and deliver the required currents and capacities above the minimum voltage after having been subjected to the following environments: random

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vibration, shock, thermal vacuum, thermal cycle, mission profile, launch pressure decay.

Planetary Protection and Cleanliness

General Cleanliness and Contamination Control requirements need to be addressed during the manufacturing and assembly of flight batteries. In addition, as a part of planetary spacecraft, the battery is subject to NASA Planetary Protection requirements, and special precautions will be taken during final assembly to limit the numbers of trapped microbes in the assembly.

An inspection of the battery is performed to show that it is free from all visible contamination such as fingerprints, particles, corrosion products, metal chips, scale, oil, grease, preservatives, adhesives, and any foreign material. Visual inspection is performed without magnification and with vision not worse than 20/30 and under a white light having an intensity 100 foot candles minimum at a distance of 6 to 18 inches. Wipe tests, water break tests, ultraviolet inspection, special lights and mirrors are considered aids to visual inspection. During final assembly, the battery components are thoroughly cleaned with iso-propyl alcohol (IPA). Battery components and cleaning materials will only be handled with gloves. Gloves will be wiped with IPA frequently while being worn. Cell to cell and cell to case junctions are sealed with JPL approved material (Kapton tape, etc.) The battery exterior will be thoroughly cleaned with IPA immediately prior to packaging for shipment. The packaging material in contact with the battery is sterile or thoroughly cleaned with IPA prior to use.

Safety

The contractor submits a Project Safety plan in addition to a Safety and Health plan. The contractor may submit existing safety plans tailored to conform to specific project requirements, if available. The contractor will need to assure the safety of personnel and hardware throughout all phases of battery development, fabrication, assembly, testing, handling and storage. All precautionary measures to prevent the inadvertent venting of an individual cell or assembled combination of cells need to be identified and implemented. Potentially hazardous conditions as well as hazardous procedures should be identified in a manner easily observed by personnel. The following additional considerations need to be addressed in the contractor's safety plan:


Electrical Safety

- Individual cells should be capable of surviving a short circuit current with a vent opening to release products.
- Current and temperature monitoring should be utilized to preclude the inadvertent venting of cells.
- Flight Battery cases should be designed to an ultimate safety factor of 3:1 with respect to the worst case pressure buildup for normal operations.

Voltage Limits

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- No cell should be allowed to discharge below the minimum voltage limits recommended by the manufacturer during discharge or charge above the maximum voltage limits recommended by the manufacturer during charge.

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General Safety Requirements: The contractor should include the following in their safety plan or as part of a procedure

- Type of Personal Protective equipment (PPE) that will be utilized during the assembly, handling and testing of the batteries.
- How the cells and batteries will be thermally monitored and thermally controlled during storage and shipping.
- Humidity measurement and control during assembly and storage.
- ESD monitoring and protective measure that will be employed.
- Type of fire suppression system utilized in those areas where batteries will be assembled and stored

Shipping and Transportation: Shipping of Lithium cells and batteries are addressed in DOT 49 CFR 173.185, which addresses specific requirements regarding items containing Lithium.

RANGE SAFETY REQUIREMENTS FOR FLIGHT TERMINATION SYSTEM BATTERIES

This section refers specifically to requirements for flight termination system batteries in launch vehicles. NASA has launch facilities in California and Florida. NASA launch programs must conform to the requirements set forth by Air Force range safety and NASA range safety.

The overall range safety document that describes the agency's range safety policy is NPR 8715.5 "Range Safety Program".


- Requirements for batteries used in a flight termination system are specified in Section 3.3.1 "Flight Termination System (FTS)" of NPR 8715.5.

Heritage Flight Vehicles (e.g. Shuttle, Atlas, and Delta)

Battery range safety requirements relating to flight termination systems are covered in AFSPC91-710 Range Safety User Requirements Manual, Volume 4-Airborne Flight Safety System Design, Test, and Documentation Requirements, July 1, 2004. However, this document fails to address lithium battery end-items. Guidance relating to lithium-battery design requirements is addressed in EWR 127-1 "Range Safety Requirements. Battery design requirements are specified in Section 3.14.3.3 "Flight Hardware Batteries" of EWR 127-1.

- Requirements for battery end item data are specified in Section 3.14.5.1 "EGSE and Flight Hardware Battery Design Data" of EWR 127-1.
- Requirements for battery test are specified in Section 3.14.4 "Test Requirements for Lithium Batteries" of EWR 127-1.

Specific guidance related to Li-ion systems is addressed in Attachment 1 to the Department of the Air Force 30th Space Wing Memorandum Dated May 2005. "Joint 45 SW/SE and 30 SW/SE

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Interim Policy regarding EWR 127-1 Requirements for System Safety for Flight and Aerospace Ground Equipment Lithium-Ion Batteries.”

New Flight Vehicles (e.g. Ares)

Battery requirements are specified in Section 3.16 “Batteries” of RCC 319-07 “Flight Termination Systems Commonality Standard”.

Batteries test and analysis requirements are specified in Sections 4.1 through 4.15 and Section 4.26 of RCC 319-07.

Battery prelaunch test and launch requirements are specified in Section 5.1 “FTS Component, Subsystem, and System Prelaunch Test and Launch Requirements” of RCC 319-07.

Batteries preflight processing and testing are specified in Section 5.2.3 “Batteries” of RCC 319-07.

Batteries prelaunch system level tests are specified in Section 5.3.4 “Non-Secure FTR System, Automatic Destruct and Fail-Safe”; Section 5.3.5 “Secure High-Alphabet Command Terminate System”; and Section 5.3.6 “Autonomous FTS End-to-End Testing” of RCC 319-07.

Range Safety requests for special battery testing are specified in Section 5.5 “Special Tests” of RCC 319-07.

Post flight analyses of batteries are specified in Section 5.6 “Post Mission Data Analysis” of RCC 319-07.

Batteries Flight Termination System Analysis requirements are specified in Section 7.1 “General”; Section 7.2 “System Reliability”; Section 7.3 “Single Point Failure”; Section 7.4 “Fractricide”; Section 7.5 “Bent Pin”; Section 7.7 “Sneak Circuit”; Section 7.9 “Battery Capacity”; Section 7.10 “Component Maximum Predicted Environment”; Section 7.11 “Failure Analysis”; Section 7.12 “Qualification By Similarity Analysis”; Section 7.14 “RF Radiation Analysis”; Section 7.17 “Automatic Destruct System Timing Analysis”; and Section 7.19 “In-Flight FTS Analysis” of RCC 319-07.

Documentation requirements are specified in Chapter 8 “Documentation” of RCC 319-07.

In addition to the general requirements of RCC 319-07, which apply to all flight termination system batteries, Li-Ion batteries have additional requirements as outlined in the memo Department of the Air Force 30th Space Wing Memorandum Dated 4 May 2005, which outlines

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additional requirements for charging/discharging, high pressure protection, voltage potential, materials, first operational use, storage, and transportation.

7. Cell/battery handling and procedures

Handling

The following are requirements for safe handling of lithium batteries:

Use of secondary lithium batteries and test procedures must be approved by the Safety Office before doing any work with lithium batteries. Assembly procedures must include, where appropriate, mandatory inspection points and step-by-step assembly instructions or drawings. Keep lithium cells under strict charge and discharge control at all times. Never put them on conductive surfaces made of metal, unless they have the appropriate conduction protection. Assemble, process, and handle lithium cells and battery packs with caution:

- Protect batteries during assembly from shorting against foreign objects using plastic bags or the original carton.
- Use spot welding, not soldering, to attach leads directly to a cell. Only qualified and certified personnel may do spot welding on lithium batteries.
- Return lithium cells and batteries to a controlled storage area in plastic or original containers when the assembly or fabrication process is interrupted or stopped for any reason other than normal shift changes.
- Make sure each lithium cell and battery has a warning label indicating that lithium is present.

Store lithium cells indoors at room temperature or lower in a dedicated, dry, well-ventilated location.

Never short-circuit lithium cells or discharge them at currents higher than the manufacturer's maximum rating.

Never overheat or burn lithium cells or expose them to temperatures higher than tests and certification allow.

Never over (force) discharge lithium cells.

Never open, puncture, or otherwise mutilate a lithium cell.

Emergency Procedures


Exposure to Electrolyte

If electrolyte gets in the eyes, flush thoroughly and continuously with water only for a minimum of 15 minutes while rolling the eyes and lifting the eyelids. Don't put any neutralizing solution in the eyes. Get medical attention immediately; Effective flushing of the eyes may require additional assistance. Call 911.

Skin Exposure to Electrolyte

If electrolyte gets on the skin or clothing, flush the affected area with copious amounts of water, and get medical attention immediately. Call 911.

Cells Leaking, Venting, or Increasing in Temperature

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If it has been determined that there was abnormal use or that cells are leaking, venting, or increasing in temperature:

- Clear the area of personnel and have qualified and properly equipped personnel remove the batteries to a safe area.
- If possible, disconnect the cell(s) electrically from associated equipment after the cells have stabilized.
- Contact the Safety Office/first responders.

Cells Rupturing

If a rupture occurs, evacuate the area and call 911. Response personnel must use air breathing equipment (such as air packs or air face masks and separate K-bottle of breathing air), rubber gloves, and chemical apron.

Lithium/Cell Fires


If a small fire occurs (special considerations for lithium cells):

- Call 911.
- Use a graphite powder or a Lith-X (Class D) extinguisher to extinguish burning lithium.
- Don't use water, sand, carbon tetrachloride, carbon dioxide, halon, or soda acid extinguishers in lithium and most cell fires.
- For most battery fires, evacuate the area and use these extinguishers only on nearby materials to prevent the fire from spreading.

On-orbit usage in crewed vehicles

The hardware provider of the battery-powered application will assess the on-orbit usage and disposal of cells and battery packs. The applicable NASA Power Systems Office must review and approve all on-orbit charging parameters, charger circuit schematics and charger usage for rechargeable battery systems. Procedures for on-orbit battery handling, storage, replacement and disposal should be well documented. Details regarding the on-orbit usage considerations are provided in EA-CWI-033. For payloads, the hardware provider should establish on-orbit processes and operational constraints for hardware inspection and checkout that is required prior to usage of the equipment on-orbit. Hardware should be stowed on-orbit in ambient stowage conditions in the "off" condition (i.e., no drain on the batteries). If the cells or battery pack are designed for on-orbit replacement when cells are depleted, the crew is to be trained to remove, visually inspect, tape, and bag the depleted cells and packs and place them in dry trash. Fresh cells or battery packs should be inspected prior to installation into the hardware. If any leakage, discoloration, or anomaly is noticed on the cells or pack, the crew should tape, bag, tag, and place the discrepant cells in non-generic trash. If there is no leakage, rechargeable cells or packs should be processed for charging. When on-orbit operations are completed, the crew should verify the hardware has been turned off and return the unit to its on-orbit storage location. For on-orbit recharging, charging parameters and charger usage is reviewed with the Payload Safety Review Panel. The on-orbit usage of the cells and battery packs in the battery-powered application will be evaluated as part of the battery design evaluation and safety approval process.

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Post-Flight Battery Cell and Pack Removal on Crewed Spacecraft

A post-flight performance evaluation of the hardware must be conducted when hardware is returned post-flight. After battery-powered hardware has been flown, the cells and battery packs are removed from the equipment. It is recommended that a post-flight ground-based performance evaluation of the hardware be conducted prior to removing the cells and battery packs. Coin cells that provide memory storage for hardware should not be removed unless performance degradation has been noted or unless signs of damage or corrosion are noted. All other cells and battery packs need to be removed from the equipment. Primary cells and battery packs will be removed, visually inspected, taped, and bagged. The removed cells and packs will be discarded or downgraded to Class III for training or other uses. Secondary cells and battery packs will be removed, visually inspected, taped, and bagged. If reflight is planned, the removed secondary cells and packs will be processed for recharging and restored to flight readiness. Once the cells and battery packs have been removed from the hardware, the batteries and hardware from which they were removed should be appropriately tagged with identification and disposal information. The text on the tag will state that the cells (or battery pack) are not to be installed before post-flight testing. The usage of this tag does not require a discrepancy report. After post-flight ground testing has been completed, an additional tag (or updated tag) should be attached indicating that the batteries have been checked and are suitable or unsuitable for reuse. The battery compartment and contacts will be inspected for any evidence of leakage or corrosion. The hardware will need to be stored (minus the cells and battery pack) in storage conditions as specified by the hardware provider. Fresh cells or battery packs will be installed (if required by the PSRP) the next time the hardware is processed for flight. The post-flight processing plan will be evaluated as part of the battery design evaluation and approval process.

Storage

Approved battery storage locations are need for storage of the batteries (when not installed in GSE or flight hardware).


Transportation

The Department of Transportation has requirements that pertain to any transportation of lithium-ion batteries. When batteries are not incorporated into flight hardware, the following restrictions apply:

- (1) Transported on publicly-accessed roadways, they shall not exceed 50% of rated charge.
- (2) When lithium content exceeds 8.0 grams per battery, transportation packaging of individual batteries shall have caution labels in accordance with CFR 173.185.

Disposal Procedures

Disposal of all batteries and related materials is handled through the appropriate Safety Office.

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8. Testing

Once a battery is chosen for a payload/application, it needs to be tested. This section provides an outline/template for preparing a comprehensive test plan. A summary checklist of things to consider when developing a test plan is also provided.

Purpose of a Test Plan

A comprehensive test plan for any project lists the necessary tests and test programs, from component development through final flight acceptance. It provides test sequence logic and test descriptions from material, part, and component to subsystem and experiment level testing. These tests are needed to

- Demonstrate the integrity of components or subsystems.
- Qualify parts not previously space qualified.
- Verify and ensure compliance with experiment performance requirements and prove flight acceptability.
- Show compliance with the appropriate project's environmental and safety requirements such as NSTS/ISS 1700.7 and Addendum.
- Ensure adequacy of support equipment for testing and servicing the experiment.
- Characterize all experimental parameters required in data processing and analyses.
- Provide sufficient experiment familiarization to the Payload Safety Organization that commitment to flight can be recommended.

Testing is a major cost and schedule driver, which is why it is important to spend the time initially to prepare a good test plan before testing begins. Test planning between prime contractors, subcontractors, and the government should start at program initiation to ensure a successful test program.

Test Plan Outline


The following is an outline of sections necessary for a comprehensive test plan for battery systems/subsystems. A good test plan can be easily altered to produce a good test report of the findings and conclusions when testing/analysis is complete.

Introduction/Purpose: Provide general information, a brief description of the tests and supporting equipment, and the reason(s) for the tests.

Applicable Documents: Provide a list of all documents and standards that apply.

Hardware/Apparatus Description and Diagram: The hardware should be described and illustrated in detail and include the following:

- facility physical description
- functional description
- instrumentation description
- electrical schematics
- data flow diagram
- test article description

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Software Tools: Describe the software tools used, including any code specifically developed, and standard software packages used.

Test Procedures, Reports, and Logbooks: Provide a list of procedures, reports, and logbooks.

Logbooks are used to trace each step and location in the test, especially when a cell or battery is relocated.

Test Requirements: Describe the requirements and criteria for the test. For example, include any environmental or clean room requirements. For complicated tests, it is recommended that a verification matrix be prepared to preclude duplication of the verification process.

Test Readiness: Verify the test readiness of the component for testing. The following need to be identified and described:

- resources/capabilities
- test preparation
- control of inspection, measurement, and test equipment
- test conductor qualification/certification
- security restrictions (if any)
- safety precautions/personnel restrictions
- test article disposal/markings

Prototype Testing (if applicable): Describe how the component will be tested at the multi-cell level for prototype testing.

Integration/System/Subsystem Testing (if applicable): Describe how the component will be integrated into a system and the testing specifically related to integration.

Qualification and Acceptance Testing: Describe in detail the intended application and the program (e.g., space shuttle or space station) requirements. Typical testing may include functional checkout (operational, cycle), environmental (i.e., vibration, thermal, thermal vacuum), electromagnetic compatibility, power quality, or others as deemed appropriate for the specific hardware and application.

The qualification of the battery involves testing the batteries to environmental and vibration levels that are at least two times higher than the mission requirements. The flight acceptance testing involves verification of battery performance by charge/discharge cycling, vacuum leak checks and vibration. The number of flight missions that the batteries will be used for, along with the location of the battery will determine the period and level of vibration. The vibration spectrum used to screen the batteries from the occurrence of internal shorts will be slightly higher than what is obtained from the calculation of mission requirements. In some cases, the qualification and certification testing will be conducted at a battery-level (i.e., on the stand-alone battery), as well as at an integrated level with the top-level assembly (i.e., with the cells or battery pack installed in the top-level assembly). For other cases, the qualification and certification testing will be conducted only at the top-level assembly.

Flight System Performance/Characterization Testing: Describe in detail the performance and characterization testing that is being performed. This includes physical characterization

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(dimensions and weight), electrochemical characterization (OCV, CCV, capacity checks), rate capability (capacities at different charge/discharge rates and different temperatures), and vacuum leak checks. Abuse tests consist of overcharge, overdischarge, external short, internal short/crush, heat-to-vent, vibration, drop, and vent and burst pressure determination. The main features that need to be understood about the battery are the fuse rating, the operational characteristics (voltage) of the overcharge and overdischarge protection switches and the nature of the protective circuitry. On the cell-level, the levels of safety incorporated into the cell need to be understood and characterized, for example, the Positive Temperature Coefficients (PTCs), Current Interrupt Devices (CIDs), the shutdown separator, etc.

Flight System Engineering Verification/Acceptance Testing: Describe the acceptance tests performed on loose cells and battery packs before the cells and packs are installed in the battery powered flight hardware.

Test Procedures: Provide detailed descriptions of the processes and procedures of how the testing will be run and the exact sequence of any tests. Accept/reject criteria must be included for all measurements taken, as well as the tolerances for these criteria. The procedures section must be written so that it is understandable by a qualified test operator or technician who is not familiar with the project. Safety precautions are integrated into the appropriate sequence in the procedure to identify any special hazards and their controls. A typical outline for this section is:

- Test Objective - overall objective for the test
- Support Hardware - other system components needed for performing the test(s) (must be calibrated, if applicable)
- Test Hardware - nomenclature, part number, serial number, and description of hardware being tested
- Support Instrumentation - meters, scopes, etc. (all calibrated, with certifications)
- Procedure Instrument Calibration: Describe any instrument calibration requirements, for example, the amp/hour watt/hour integrator and power supplies.

Data and Analyses and Test Results/Conclusions: Record and describe any anomalies and /or any test stoppages. Identify trends and provide any calculations/equations used to derive results and conclusions.

Pre-Launch Checkout Tests: Describe any pre-launch checkout tests that need to be performed, such as power-on, basic functions, calibrations, etc.


Test Plan Checklist

The following is a summary checklist of things to consider in development of the test plan:

Principal risk areas/measures of effectiveness

Characteristics of the test plan:

- Identifies all developmental tests at system and subsystem levels.
- Identifies prime, subcontractor, supplier, and government tests.
- Identifies qualification by similarity of subsystems and assemblies.

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Define how testing is optimized:

- Define test requirements verification matrix to preclude duplication of the verification process.
- Review design analysis results to determine where verification testing is needed.
- Ensure that testing is done at the appropriate component level.
- Acceptance testing is not done unless enough parts are available for a complete configuration.

Ensure that test schedules allow time for redesign and retest.

Provide contingency resources for unforeseen test problems.

Use proven testing techniques, especially when accelerated testing is planned.

Ensure that design changes are verified during reliability development testing.

TESTS

The following sections list typical testing requirements.


Qualification Testing should demonstrate that the design, manufacturing process, and acceptance program produce battery hardware that meets specific requirements with adequate margin and validate the planned acceptance program including test techniques, procedures, equipment, instrumentation, and software. Each type of battery, module, or cell design that is to be acceptance tested will also have a corresponding qualification test. A qualification test specimen should be exposed to all applicable environmental tests in the order of the qualification test plan.

Test Hardware is produced from the same drawings, materials, process, and level of personnel competency as used for flight hardware. Ideally, the test article would be selected from a group of production items.

Environmental tests stress the hardware beyond the maximum conditions it will see. Should not exceed design safety margins or cause unrealistic modes of failure. The qualification test conditions should include those of all possible missions.

Tests performed should include Inspection, Specification Performance, Leakage, Shock, Vibration or Acoustic, Acceleration, Thermal Cycle, Thermal Vacuum, Climatic, Proof Pressure, Electromagnetic Compatibility, Life, Burst Pressure, Static Load, and Safety and should follow MIL-STD 1540E.

Life qualification tests should confirm battery and battery module life expectancy. Confirmation of battery life expectancy is based upon battery life testing or a combination of analyses and confirmation of the life expectancy of battery materials and components, such as module, cell, electrical bypass devices, heaters, strain gauges, temperature sensors, or thermal switches. Confirmation of battery module life expectancy is based upon module life testing or a


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combination of analyses and confirmation of life expectancy of module materials and components, such as cell, electrical bypass devices, heaters, strain gauges, temperature sensors, or thermal switches. Confirmation of life expectancy of battery components is based on life testing. Life testing of battery, module, or cell for service life expectancy confirmation is under a set of conditions that envelop the conditions preceding launch, mission battery loads, charge control methods, and conditions and temperatures. Test equipment and fixtures should maintain flight-like thermal and mechanical configuration such as simulating flight-like temperature variations and external compression. Test duration should include margin to demonstrate the required battery reliability and confidence level from the number of test samples. For spacecraft applications, a battery, module, or cell life test used to confirm life expectancy can be a real-time life test where the real-time data is from on-orbit or real-time ground tests where the time, current, and temperature profiles of discharge and charge exactly match those of the mission. The data should envelope flight-level cell matching criteria and incorporate flight-like charge control methods. Data from real-time tests should include electrical performance data and data from destructive physical analysis of tested cells. Alternatively, for spacecraft applications, a battery, module, or cell life test used to confirm service life expectancy can be a set of time-accelerated tests that envelopes the mission loads, charge control methods, and conditions and temperatures. The acceleration factor can have different values for storage, cycling or at different operational modes. The acceleration factor is confirmed by real-time life test data where the time, current, and temperature profiles of discharge and charge exactly match those of the mission. Real-time data includes on-orbit data or data from real-time ground tests that envelope flight-level cell matching criteria and incorporate flight-like charge control methods. Data from real-time and accelerated tests should include electrical performance data and data from destructive physical analysis of tested cells. The acceleration factor is based on a sound analysis of data and should not be greater than two. Real-time and accelerated life test durations include margin to demonstrate the required reliability and confidence level from the number of test samples and failure rate characteristics.

Selection of a new cell design without real-time data demonstrating mission life increases risk to the spacecraft program. The following are ways to minimize program risk:

Pursuit of a dual-path approach with a more established design or technology

Battery sizing with the new technology will need to be designed with a greater EOL energy margin. A rationale for determining this factor should be provided and final approval will be made by the procurement authority. Results from destructive physical analysis of the cells on real-time life tests is used to evaluate degradation modes prior to launch. Time-accelerated test data can facilitate risk assessment as a method to define possible failure mechanisms and trends. Results from destructive physical analysis should be provided. The decision to include a new technology or design for a mission before there is sufficient data to conclusively verify mission life may be made, with the exception that ground testing will continue until mission life margin is demonstrated.

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The real-time life test sample size needs to provide a minimum of 90% confidence level at 88% reliability (or 20 cells) without failure. Other sample sizes can be used. If the sample size, N , is not 20, the actual test duration without failure should be multiplied by a factor K for mission life expectancy. The reliability and confidence level will need to remain at 90%/88% for a test with N samples without failure for duration KT . If the failure probability function is not known, the use of a Weibull function is suggested to establish test durations. The beta shape parameter should be estimated from failure data of the most comparable cells and operational type conditions. As more data are accumulated, a failure probability function can be refined.

Storage, and cycle test history should be available for each individual life test sample down to the cell level. Cell level (module level and battery level, as applicable) acceptance test data will be defined at minimum individual cell capacity to minimum useable voltages, charge retention, and impedance at defined conditions. Beginning of test mission capacity and voltage profile measurements will be defined that define total available capacity at mission operating conditions to minimum useable voltage at the cell level, module level, and battery level, as applicable. End of test mission performance measurements will be compared with “Cell level...” and “Beginning of test...” at the cell level, module level, and battery level, as applicable. Periodic energy measurements can be performed during the life test to facilitate performance trending. If energy measurements are performed, capability for on-orbit reconditioning need to be available, unless life test data and statistical analysis is provided, conclusively demonstrating that mission life and reliability requirements can be met without it.

The life test cells are built to an approved set of manufacturing control documents, which defines the qualified cell design. The procuring authority has the right to review manufacturing control documents to confirm that the flight lot cell design is identical to that of the life test cell.

Safety testing validates battery-level safety against all known failure modes. Battery-level safety is validated by test to the following conditions, at minimum: overcharge, overdischarge, over temperature, over pressurization, internal cell short, and external cell short. If a battery-level safety analysis is performed, cell, module, or battery-level development testing should be provided that simulates battery mechanical and thermal design, and evaluates the potential of one cell failure propagating to another cell or piece part within the battery.

For NASA Glenn Research Center Payloads:

Qualification Tests

These tests are typically performed only on flight qualification units and require quality assurance personnel certification/witness signoff and formal configuration control:

- Physical and electrochemical characteristics: Dimensions, weight, OCV, CCV, capacity checks
- Environmental test:

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- Charge and discharge at temperatures that are 20°F above and below actual temperatures seen during operation. For example, batteries used for IVA (intra-vehicular activity) (in-cabin) will be tested at 50 and 90°F. Storage locations of the battery during flight are an important factor.
- Vacuum exposure: Six hours at 0.1 psi. Requires specific rates of depress and repress; weight and functional checks to be performed.
- Vibration: Fully charged battery packs are vibrated using the qualification spectrum for 15 minutes in each of the x, y, and z axes.

Frequency Level

20-80 Hz +3 dB/octave

80-350 Hz XXX g²/Hz (dependent on chemistry and stowage)

350-2000 Hz -3 dB/octave

- OCV checks in between each axis of vibration and functional check after the vibration to determine when/if cell/battery failures occurred during or after completion of this test.

Flight Acceptance Tests

Batteries are required to undergo physical and electrochemical characterization with pass/fail criteria. Quality assurance signoff and formal configuration management is also required for flight acceptance tests.

- Vacuum leak check as described earlier with pass/fail criteria for post functional checkout and weight change.
- Vibration test: Fully charged battery packs vibrated in each of the x, y, and z axes using flight acceptance test spectrum. For Li-ion, only voltage monitoring is performed. OCV is checked between each change in axis of vibration.

Frequency Level

20-80 Hz +3 dB/octave

80-350 Hz X g²/Hz – (depends on chemistry and location stowage)

350-2000 Hz -3 dB/octave

Functional checks are performed after the vibration.


For JPL planetary applications:

Acceptance tests

Capacity at 20°C

The battery will be charged to battery end-of-charge voltage at C/5 or until 1st cell reaches maximum cell voltage then tapered until the current reaches the C/50 rate. Discharge at C/5 to battery end-of-discharge voltage.

Capacity at -20°C

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The battery will be charged to end-of-charge voltage at C/10 or until 1st cell reaches maximum cell voltage then tapered until the current reaches the C/50 rate. Discharge at C/5 to end-of-discharge voltage.

Capacity at 0°C

The battery will be charged to end-of-charge voltage at C/5 or until 1st cell maximum cell voltage then tapered until the current reaches the C/50 rate. Discharge at C/5 to end-of-discharge voltage.

Capacity at 30°C

The battery will be charged to end-of-charge voltage at C/5 or until 1st cell reaches maximum cell voltage then tapered until the current reaches the C/50 rate. Discharge at C/5 to end-of-discharge voltage.

Battery Charge Retention at 20°C (pre and post environ. Testing).

All batteries have the following requirements and conditions as defined at a test temperature of 20°C: Charge at C/10 to end-of-charge voltage or maximum cell voltage/ 1st Cell; open circuit stand for 72 hrs; Discharge at C/5 to end-of-discharge voltage; Requirement: No more than 35-mV/ cell loss in from 2nd to 72nd hour on open circuit.

Battery Impedance

The Impedance of each battery will be determined at 100 and 50%, state of charge at -20, 0, and 20°C using a pulse technique, then calculating the $\Delta V/\Delta I$ values. The impedance of all batteries needs to be less than 100 Milliohms at 20°C.

Battery Isolation

The cell cases are electrically insulated from each other, heat sinks, and from the battery housing. The DC resistance between cells and all support hardware, heat sinks, battery base plate, etc. is greater than 10 mega ohms when tested at a voltage of 50 Vdc. Isolation resistance between the battery wiring and the battery housing is greater than 100 K ohms when measured with a Simpson Meter or equivalent.

Qualification Tests

Random Vibration

The battery should be designed to withstand the vibration levels shown in the following table. The qualification battery is tested at acceptance levels for 1 minute per axis followed by qualification levels at 2 minutes per axis. The remaining flight and spare units are then tested at flight acceptance levels of 1 minute per axis. The vibration test levels is applied to the battery at the mounting points in each of the three mutually orthogonal axes. Random vibration levels (derived from acoustic and launch vehicle transient vibration spectra) are defined at the rover-mounted equipment interface given in the following table and again graphically in the figure below. The battery is powered-on during vibration testing, if required to operate during launch. However, for improved anomaly perception, powered on vibration is strongly encouraged for all units regardless of operational requirements during launch.

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Random Vibration at Rover/Equipment Interface

Frequency (Hz)	Acceptance level (g^2/Hz)	Qual. Level (g^2/Hz)
20-80	+ 6db per octave	+ 6 db per octave
80 – 450	0.04	0.08
450-2000	-6 Db per octave	- 6 Db/ octave
Overall	5.5 g_{rms}	7.8 g_{rms}

Shock (Pyro-shock)

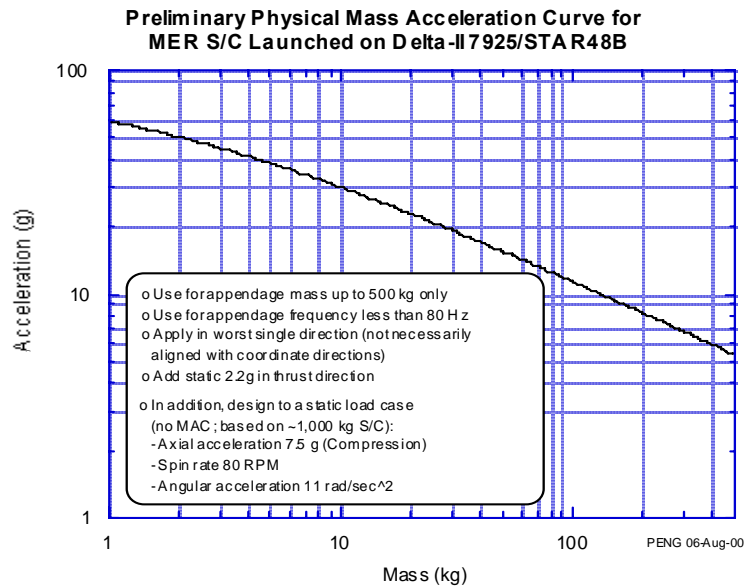
The Li-Ion rechargeable battery on the Rover, considered in Zone 2, should be designed to operate after being subjected to two (2) pyro-shocks in each of three orthogonal axes at the levels shown below in the following table.

Pyro-shock levels

Frequency (Hz)	Qual, Peak SRS Response (Q=10)
100	20 g
100-1600	+ 10 dB per Octave
1600-10,000	2000 g

Structural Loads Landing Loads

The batteries are designed to withstand a quasi-static limit landing load of 40g. Test margin of landing load is 1.2.



Acceleration and Limit Design Loads

Flight Hardware Factors of Safety (FS)

Structural analysis of flight hardware will use the following yield and ultimate factors of safety consistent with the item's structural test option (See the following table).

Structural Analysis Factors of Safety^{a,b,c,d}

	Tested Structure	Non-Tested Structure
Yield	1.25	1.60
Ultimate		2.00


Thermal Vacuum Requirements (For batteries)

a. Pressure – The pressure is to be reduced from atmospheric to 10⁻⁵ Torr or less.

b. Temperature – The component temperature range to be used in thermal vacuum testing is defined in the following table. The temperature is stabilized at each specified temperature prior to initialization of electrical testing. Eight thermal cycles are required of which only the first and last cycles need to be under vacuum and require electrical testing.

Qualification Temperatures

During Cruise	-30 to 40°C
Charge on Mars	-10°C to 40°C
Discharge on Mars	-30 to 40°C

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Thermal Cycle Requirements

Each battery in the battery unit will be tested and monitored. The temperature range to be used in thermal cycle testing is -20 and $+40^{\circ}\text{C}$. The temperature is stabilized at each specified temperature prior to initialization of electrical testing. Eight thermal cycles are performed on the Qualification battery. On the final cycle the capacity tests shown in the following table are repeated. The capacities need to meet the BOL battery capacity requirements as described in the requirements except for the required capacity at 40°C , which would be the same as 20°C .

Thermal Vacuum Test Conditions

	Description
20°C	Charge at 0.8 A to $32.8\text{V}^{(a)}$ then taper to 0.32A. Discharge at 0.8 A to cutoff voltage of 24V or first cell to 3.0V. Recharge to $32.8\text{V}^{(a)}$ then taper to 0.32A.
0°C	Discharge at 0.8 A to cutoff voltage of 24V or first cell to 3.0V Charge at 0.8 A to $32.8\text{V}^{(a)}$ then taper to 0.32A
-20°C	Discharge at 0.8 A to cutoff voltage of 24V or first cell to 3.0V Charge at 0.8A to $32.8\text{V}^{(a)}$ then taper to 0.32A
-30°C	Discharge at 0.8 A to cutoff voltage of 24V or first cell to 3.0V
$+40\text{C}$	Charge at 0.8A to $32.8\text{V}^{(a)}$ then taper to 0.32A Discharge at 0.8 A to cutoff voltage of 24V or first cell to 3.0V Charge at 0.8A to $32.8\text{V}^{(a)}$ then taper to 0.32A
20°C	Discharge at 0.8 A to cutoff voltage of 24V or first cell to 3.0V Charge at 0.8 A to $32.8\text{V}^{(a)}$ then taper to 0.32A .Repeat discharge at 4A and 8A. Charge at 0.8 A to $32.8\text{V}^{(a)}$ then taper to 0.32A
Thermal Cycle	Repeat Thermal cycle 8 times without electrical testing
8 th Cycle	Repeat all electrical measurements as performed for Thermal/Vac on Cycle 1

Note: Charge switches to taper at 32.8 V or when first cell reaches 4.15V

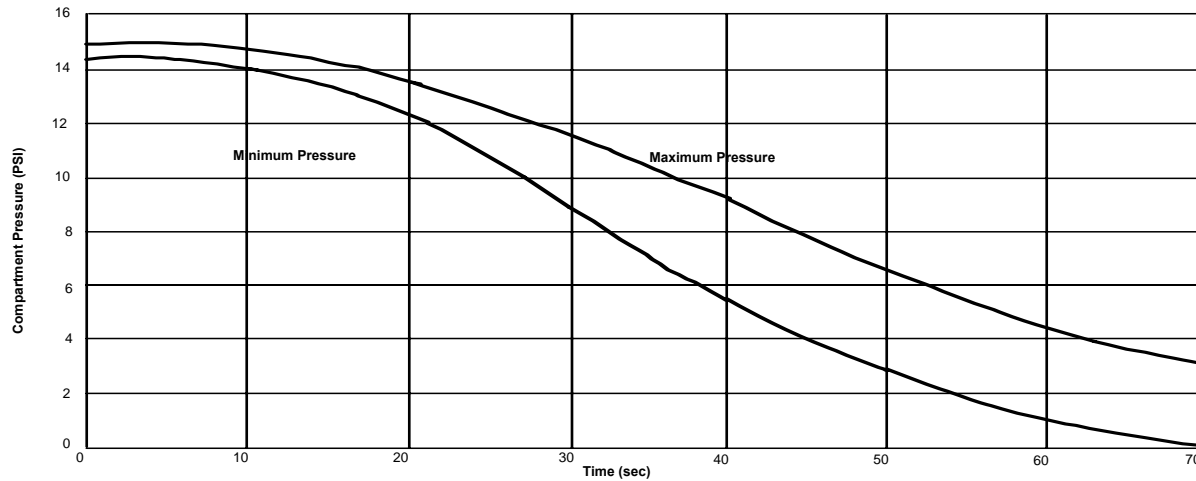
Profile Test

Testing will be performed to the specific mission profile.

Launch Pressure Decay

The battery should be designed for payload fairing venting as shown in the following figure at a pressure decay rate of 33 Torr/sec and shown by analysis.

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CELL SCREENING TESTS


This section provides a summary of the screening tests that can be performed to match cells for use in a battery system. Cell matching must be performed regardless of the battery chemistry chosen or the qualification/acceptance testing to be performed.

Automated Testing Equipment for Single Cells

Automation of battery testing is advantageous when time is of the essence. Automated cycling of cells can be accomplished by using the cell operating voltage lower and upper limits. The maximum allowable voltage according to the battery manufacturer is used for the end of charge voltage cutoff. The manufacturer's suggested minimum voltage should be used as the end of discharge cutoff. Once a cell has been activated and burned in (if required), the cell should not be discharged below the minimum cutoff voltage or charged above the maximum cutoff voltage. A constant current, constant voltage power supply is used to both charge and discharge the test cell. Discharging can also be accomplished through a resistive load. Depending on the type of cell being tested, it may also be desirable to perform cycles where the charging and discharging are periodically stopped for a measurement of open circuit voltage. This can be useful in characterizing the amount of state-of-charge/discharge hysteresis that is occurring. Usually this is minimal, but if hysteresis is present, 50 percent state-of-charge (SOC) and 50 percent depth-of-discharge (DOD) are not occurring at exactly the same point.

Coulombic Efficiency Determination

An amp-hour integrator is used to measure the constant current charge and constant current discharge capacity of the cell(s). The ratio of the discharge capacity to the charge capacity gives the efficiency for a particular cycle. Factors that affect coulombic efficiency include excess gas evolution (usually hydrogen), development of a short circuit between anode and cathode, separator fouling or perforation, and irreversible chemical reactions. Cycles like these are

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required to be able to determine state-of-charge and depth-of-discharge. If a large number of cycles are performed, such as in a life test, a determination of useful life can be made.

Polarization Testing


The electrochemical activity of a cell should be determined periodically by measuring its voltage-current relationship. These tests are performed by applying the required current (5 or 6 different current settings within the capabilities of the cell used should be chosen) in charge mode for about 20 seconds and then in discharge mode for about 20 seconds. (Note: Exceeding the rated current carrying capability of a given cell can lead to permanent damage even for short term exposures such as this. Choose test current density values carefully). In this way, the cell state-of-charge should remain approximately the same at the end of the test as it was at the beginning of the test. This test should be done at 25, 50, and 75 percent SOC. The degree of linearity of the plotted data (voltage as a function of current density) indicates whether the electrode is exhibiting kinetic or concentration polarization effects. Kinetic effects and poor mass transport properties are evidenced by non-linearities at low and high current densities. The internal resistance of the cell can be calculated by determining the slope of the discharge curves at each of the states-of-charge. Cell resistance can also be measured with an impedance bridge at 1000 Hz. This measurement generally is in good agreement with the resistance calculated from the slope of the voltage-current relationship.

Open Circuit Decay Test

This simple test involves stopping during charge and/or discharge cycles at specific intervals (usually based on SOC), and observing the rate of decay for a fixed time interval. Usually 25, 50, and 75 percent SOC are chosen for convenience. Cells with steeper decay rates should be eliminated from consideration.

Tailoring Screening Tests

Screening tests can be tailored to individual cell types. A series of combination cycles can be run which would allow the engineer to graphically observe deviations in cell behavior. For example, 1.5 Ampere hour Lithium ion cells can be cycled in the following way for screening purposes. By analyzing the plotted data, performance differences can be easily seen. Begin with a C rate charge at anything from C/1 to C/10 to a maximum of 4.2V. Then switch the cell to open circuit (or wait state) for a short period of time (usually for several minutes; the same wait time should be used for all cells of the same type). At the end of the wait state, observe and note the voltage decay, and then do the following special discharge: Discharge at C/1 for 1 minute, then without hesitation, switch to a C/10 discharge down to 2.4 volts. All graphical data should be plotted using the same scale values. The resulting voltage vs. time curve should be an upward sloping charge curve with the expected peaks, followed by a self discharge dip or notch, attached to a steep downward curve that abruptly turns upward caused by the reduction in the discharge rate. The difference between the C/1 discharge and the upturn resulting from the abrupt decrease in discharge rate allows the internal resistance of the cell to be determined. Finally, after the initial rise, the discharge curve decreases back down into a more

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typical slope. Continue to test the cells in question for about 50 cycles. After about 50 of these special cycles, analyze the data to pick out cells that can be assembled into a string of cells.

THERMAL TESTS

Cells and batteries should be tested in an environment that is as close to the intended application as possible. Thermal environment in particular is a factor that significantly affects how a battery will perform. Most cells function more efficiently at warmer temperatures rather than cold. Depending on the cell type, batteries may require active thermal management (circulating coolant), passive thermal management (insulation or heat sink), or a special location (waste heat conducted from nearby electronics). Frequently, more cells are required in a battery that will be operating in a low temperature environment. Consult the manufacturer of the cells to determine known behavior at low and high temperatures. If the manufacturer has not performed testing at the temperature of interest, thermal screening tests will be needed for the temperature range in question.

COTS MULTI-CELL BATTERY TEST PROGRAM

NASA Johnson Space Center (JSC) has a stringent test program for testing new Commercial-Off-the-Shelf (COTS) batteries (string of COTS cells). There are three major parts of the test program: (1) engineering/certification test; (2) qualification test of batteries; and (3) flight acceptance test. The engineering certification test requires testing individual cells and the battery for performance and abuse. The qualification test includes environmental testing. JSC can perform this test program for projects if requested. In addition, JSC may already have gathered considerable test data for the type of battery/cells being considered by the project. A request for this type of historical data may allow a project to dispense with some of the testing outlined below.


Engineering/Certification Tests

Engineering/certifications tests are performed primarily to eliminate those batteries with workmanship problems, and to gain familiarity with the behavior of the battery as an assembly of a string of individual cells.

Battery Level Performance Testing

The following are key battery level performance tests:

- Open Circuit Voltage (OCV) measurement of “as obtained” batteries
- Constant Capacity Voltage (CCV) - load equivalent to 1.5 C current for 100 ms pulse
- Functional performance of battery by performing in-situ testing or by mission simulation; some cells perform differently in a battery system than as individual cells
- Thermal environment – performance of batteries at 20°F above and below flight operational environment
- Vacuum leak check – to check for leakage and tolerance for up to six hours of exposure to vacuum environment


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- Leak check on 100% of flight batteries - qualification/certification test is performed on engineering and qualification hardware.
- Vibration – batteries and cells are vibrated to determine vibration tolerance to launch and descent. Test vibration is very much dependant on launch and landing environments, number of missions, and cell chemistry.
- Used as a screening method for workmanship standards.
- Used as a screening method for internal shorts in some lithium primary and all Li-Ion cells/batteries.
- Typical vibration spectrum for qualification is at least five times higher than that for flight acceptance and at longer than flight durations. Acceptance vibration is performed on 100% of flight batteries to screen for internal shorts and/or workmanship defects.

Abuse Tests

The following are key battery level abuse tests for battery screening and matching:

- Overcharge
 - Typical failures: charger failure; protective circuit board failure
 - Cell level: 3C rate fast charge, over-voltage (to 5.0 V for Li-ion); overcharge to 12.0 V for 50 minutes (UL test)
 - Battery level: verify protective feature for overcharge/over-voltage
- Overdischarge test
 - Typical failures: low-voltage cutoff (in equipment) failure; protective circuit board failure
 - Cell level: fast discharge at 3 C rate; discharge into reversal
 - Battery level: Characterize low voltage cutoff switch setting; verify logic in circuitry to determine if individual cell voltage or total battery voltage opens the safety MOSFET switch
- External short circuit test
 - Typical failures: inadvertent shorting across terminals; hard-blow/thermal fuse failure; protective “smart” circuit board failure; multi-switch failure
 - Cell and battery level: external hard short is deliberately imposed on the battery under carefully controlled conditions
- Internal short circuit test (crush)
 - Presence of impurities (metal burrs, particles, dust) that can be dislodged due to vibration (manufacturing defect) are common causes of short circuits
 - Simulated internal short using a crush method.
- High temperature and heat-to-vent

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- Temperature tolerance on cells and determination of thermal runaway temperatures
- Requires cells be well instrumented with thermal measuring devices
- Drop/Shock test
 - Simulates problems encountered during ground handling and transportation – inadvertent drops
- Vent and burst pressure test
 - Vent/burst pressure ratio ≥ 2.5
- Destructive Physical Analysis (DPA) with electrolyte analysis
 - For toxicology assessment and report (independent materials usage and toxicological memos required)

VIBRATION TESTING AND TOLERANCE TO INTERNAL SHORTS

Since the absence of internal shorts cannot be proven with confidence, a screening method has been developed at NASA-JSC-EP5 for the removal of cells/batteries with this type of defects. The cells/batteries are tested to prove tolerance (no venting, fire or explosion) to internal shorts using simulated methods. If such tolerance is not observed, batteries and cells are screened with a level of vibration that is higher than workmanship levels (see above paragraphs on testing batteries that are intolerant to internal shorts). The vibration spectrum may also be determined by the hardware provider in conjunction with the Power Systems Office battery evaluator.

Qualification Vibration Testing (QVT) for Batteries Tolerant to Internal Shorts

The purpose of the qualification vibration test for those batteries that are tolerant to internal shorts is to demonstrate the ability of the component to withstand the stresses and accumulated fatigue damage resulting from the maximum random vibration environment. The test duration in each of the three orthogonal axes is equivalent to either the total acceptance vibration test time the battery will experience or five minutes, whichever is greater. The test levels and spectrum are shown in the following figure and table.

Test condition tolerances are applied to the nominal values defined in the following figure and table. A maximum allowable tolerance of ± 1.5 dB is applied to the Power Spectral Density values. Any aspect of the test not specifically defined in this document will be conducted in accordance with the applicable requirement.

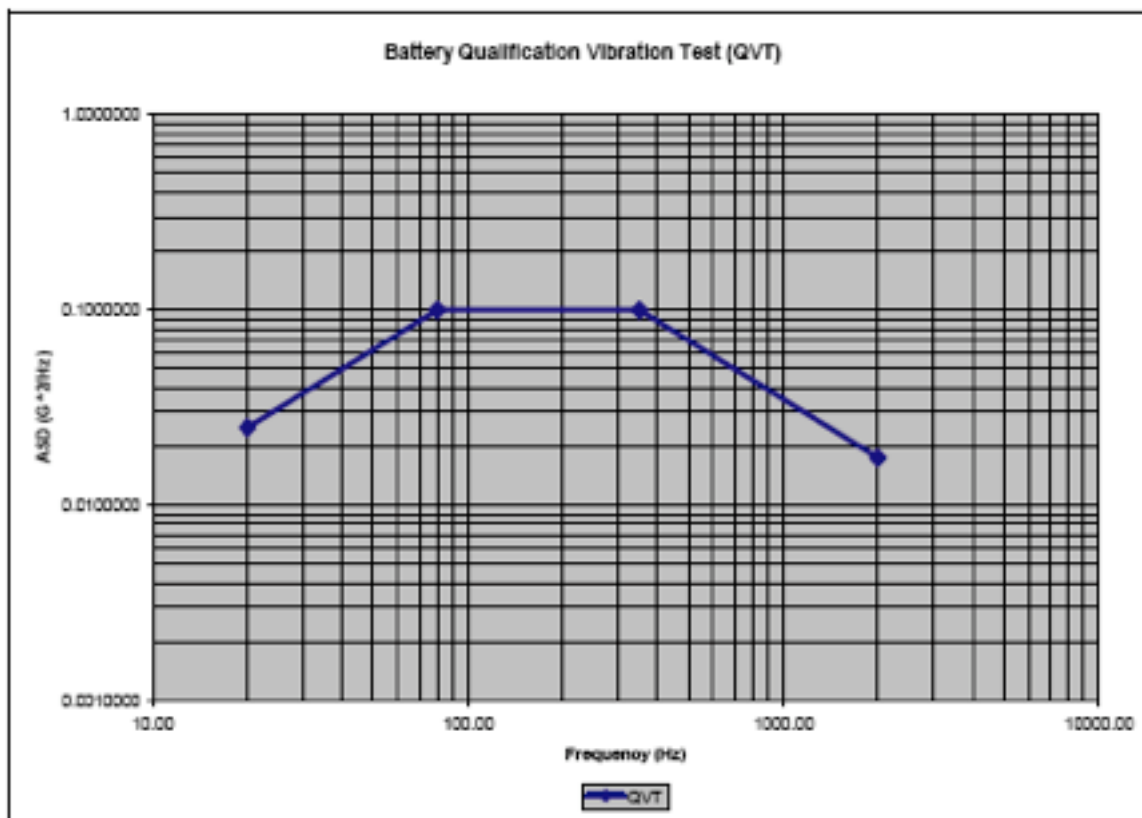


Figure Qualification Vibration Spectrum for Batteries and Cells Tolerant to Internal Shorts

FREQ (Hz)	ASD (G ² /Hz)	dB/OCT	Grms
20.00	0.025000	*	*
80.00	0.100000	3.01	1.94
350.00	0.100000	0.00	5.55
2000.00	0.017500	-3.01	9.58

Table Qualification Vibration Spectrum for Batteries and Cells Tolerant to Internal Shorts

Qualification Vibration Testing (QVT) for Batteries Intolerant to Internal Shorts

The purpose of the qualification vibration test for those batteries that are “intolerant” or “not tolerant” to internal shorts is to demonstrate the ability of the component to withstand the stresses and accumulated fatigue damage resulting from the maximum random vibration environment and to identify any potential internal short hazard. The test duration in each of the three orthogonal axes are equivalent to either the total acceptance vibration test time the battery will experience or five minutes, whichever is greater. The test levels and spectrum are shown in the following figure and table and are applicable only to batteries being launched in the following locations: Shuttle middeck, MPLM, Progress and Soyuz. The only exception is that batteries cannot be launched in the Progress/Soyuz descent module under any circumstances.

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Test condition tolerances are to be applied to the nominal values defined in the following figure and table. A maximum allowable tolerance of +/-1.5 dB is applied to the Power Spectral Density values. Any aspect of the test not specifically defined in this document will be conducted in accordance with the applicable requirement.

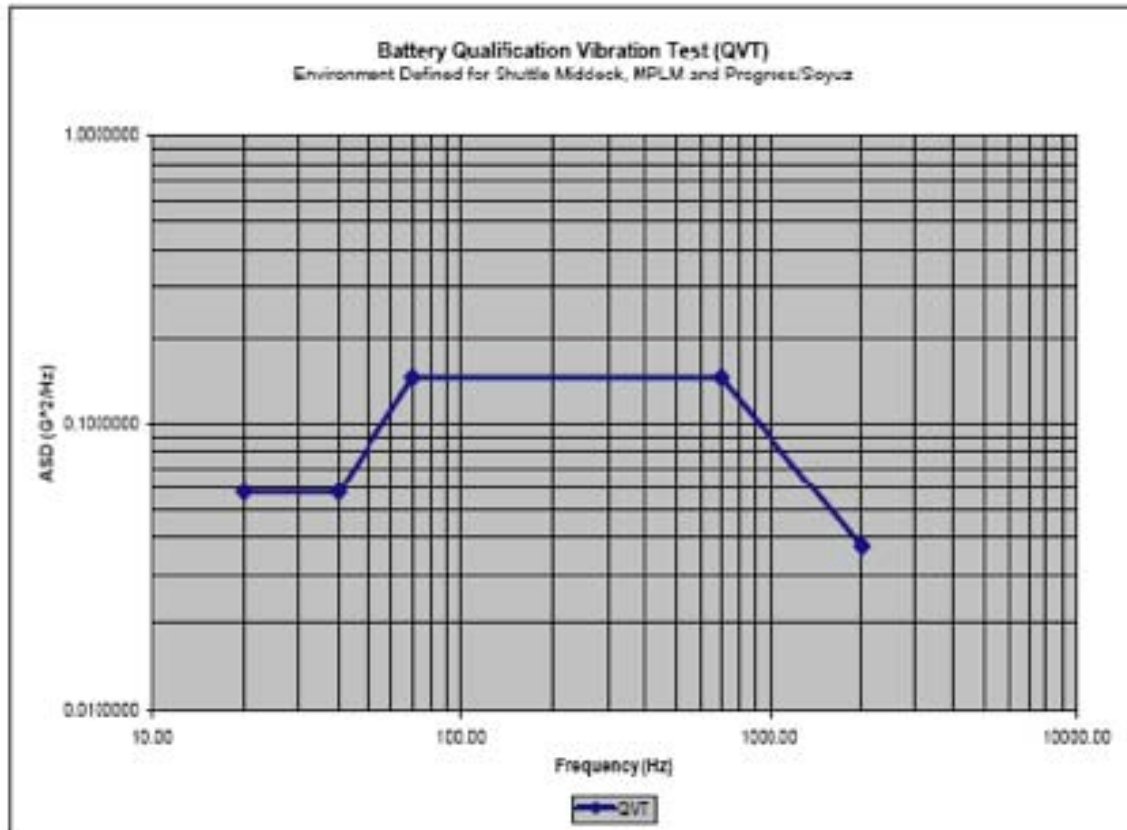



Figure Qualification Vibration Spectrum for Batteries Intolerant to Internal Shorts


FREQ (Hz)	ASD (G ² /Hz)	dB/OCT	Grms
20.00	0.057600	*	*
40.00	0.057600	0.00	1.07
70.00	0.144000	4.93	2.02
700.00	0.144000	0.00	9.74
2000.00	0.037440	-3.86	13.65

Table Qualification Vibration Spectrum for Batteries Intolerant to Internal Shorts

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Appendix A: Definitions

Battery

A Battery is an assembly of battery cells or modules electrically connected (usually in series) to provide the desired voltage and current capability. Generally, the cells are physically integrated into either a single assembly (or battery) or into several separate assemblies (or modules). A battery may also include one or more attachments, such as electrical bypass devices, charge control electronics, heaters, temperature sensors, thermal switches, and thermal control elements.

Calendar Life


The calendar life of a cell or battery is the maximum allowed period of use of the cell or battery as defined from the date of manufacture of the oldest cell in the battery.

Capacity

Battery Capacity is measured in units of Ampere-hours (for Ah capacity) or Watt-hours (for Wh capacity). Battery capacity is equal to the integral of the discharge current, where I_d is a positive value. The limits of integration are from start of discharge to either the minimum power subsystem battery voltage limit, or when the first cell reaches the lower cell voltage limit, or when a defined time duration is reached. This is a point-in-time capacity value that is measured at a defined charge voltage-current profile, discharge load profile, and temperature profile.

$$\text{Battery capacity (Ah)} = \int I_d dt$$

$$\text{Battery capacity (WH)} = \int I_d V_d dt$$

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Cell (or Battery Cell)

A cell is a single-unit device within one cell case that transforms chemical energy into electrical energy at characteristic voltages when discharged. Battery cells can be connected (usually in series) to form a battery. Battery cells can be connected in series or parallel to form a module; in such cases, the modules are connected (usually in series) to form a battery.

Cell Activation

The addition of electrolyte to a battery cell constitutes cell activation and starts the clock on cell, module, and battery service life. It is used to define the start of battery shelf life. Li-ion cells are activated at the manufacturing facility during cell production. Following activation, Li-Ion cells typically undergo several charge/discharge cycles to condition the surface of the electrodes and stabilize capacity.

Cell Design

A cell design is built to one set of manufacturing control documents that define material composition, dimensions, quantity, process, and process controls for each component in the cell. A change in cell design is considered a different cell design that requires a separate qualification. A change in cell design includes, but is not limited to, the following:

- Positive electrode composition, raw material (including binder), loading density, foil, dimension, or process change
- Negative electrode composition, raw material (including binder), loading density, foil, dimension, or process change
- Electrolyte composition
- Separator composition or dimension
- Cell stack dimension or composition
- Cell case size
- Change in cell or raw material manufacturing location
- Terminal seal


Cell Lot

A cell lot is a continuous, uninterrupted production run of cells, which consists of an anode, cathode, electrolyte material, and separator, from the same raw material sublots with no change in processes or drawings. Li-Ion cells produced in a single lot should be procured, stored, delivered, and tested together to maintain single lot definition.

Charge/Discharge Current C/n (or C-rate)

The constant charge or discharge current for a battery is defined as C/n, or C-rate. C is the cell-level rated (or nameplate) capacity in Ampere-hours (per vendor's criteria), and n is any value for elapsed time measure in hours. For example, a discharge current of C/2 for a 20 A-h rated cell is a discharge current of 10 A.

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Cold Storage

Cold storage, for batteries that are not in use, is long-term storage where the temperature and humidity environments are controlled, and temperature is below ambient temperature.

Cycle Life

The number of discharge/charge cycles performed by the battery.

Depth of Discharge (DOD)

The ratio of the number of Ampere-hours removed from a battery for a defined charge voltage-current profile, discharge load profile, and temperature profile to the battery rated (or nameplate) capacity E(Ah), times 100. For a Li-Ion battery, the DOD must be specified at a state-of-charge operation or a voltage that relates to state-of-charge operation.

$$\text{Battery Depth-of-Discharge (\%)} = [E(\text{Ah}) \text{ removed} / E(\text{Ah}) \text{ rated}] * 100$$

Note: For batteries that are subcharged, i.e., not recharged to full energy, DOD is the percentage of energy expended in a discharge from the subcharged point. For example, a battery that is subcharged to 70% SOC and then cycled down to 40% SOC is considered to have cycled over 30% of its energy, and the DOD is 30%.


Energy

Launch, transfer orbit, and on-orbit battery energy and energy reserve requirements are flowed down from the Electrical Power Subsystem specification for the entire mission life. Battery energy is equal to the integral of the product of discharge current and voltage, where I_d , a positive value, is the discharge current, and V_d , a positive value, is the discharge voltage. The limits of integration are from start of discharge to either the minimum power subsystem battery voltage limit, or when the first cell reaches the lower cell voltage limit, or when a defined time duration is reached. This is a point-in-time energy value that is measured at a defined charge voltage-current profile, discharge load profile, and temperature profile. Battery discharge can be accomplished with constant current discharge; however, constant power discharge is the preferred method if it more closely simulates spacecraft power. This is also sometimes called Watt-hour capacity.

$$\text{Battery Energy (Wh)} = \int I_d V_d dt$$

Energy Reserve

Total amount of usable energy in Watt-hours remaining in a battery, which has been discharged to the maximum allowed DOD under normal operating conditions to either the minimum power subsystem battery voltage limit, or when the first cell reaches the lower cell voltage limit.

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Note: Energy reserve provides enough energy to ensure positive energy balance during the maximum sun-outage time when a loss of attitude control occurs coincident with the end of the longest eclipse. Energy reserve may also be used for other rare, deep discharges such as relocation with electric propulsion, or those that may occur in transfer orbit.

Maximum Expected Operating Pressure

The maximum pressure that pressurized hardware is expected to experience during its service life, in association with its applicable operating environments.

Module (or Battery Module)

A battery module is an assembly of series- or parallel-connected battery cells that are connected (usually in series) to form a battery.

Procurement Authority

The agency responsible for the procurement of the spacecraft.

Rated or Nameplate Capacity

The rated or nameplate battery capacity is measured in units of Ampere-hours or Watt-hours. The rated battery capacity is provided by the battery or cell vendor and is typically less than the actual capacity. Manufacturers usually provide excess capacity over the rated value to compensate for variability within the manufacturing lot and capacity losses expected over the life of the battery.

Service Life

The service life of a battery, battery module, or battery cell starts at cell activation and continues through all subsequent fabrication, acceptance testing, handling, storage, transportation, testing preceding launch, launch, and mission operation.


Shelf Life Limit

Shelf life limit for a battery, module, or cell is the maximum allowed time from cell activation to launch. This includes any time in cold storage.


State of Charge

The ratio of the number of Ah or Wh present in a battery for a defined charge voltage-current profile, discharge load profile, and temperature profile to the rated energy E(Ah or Wh) of the battery, times 100.

Battery State-of-Charge (%) = $[E(\text{Ah or Wh}) \text{ present} / E(\text{Ah or Wh}) \text{ rated}] * 100$

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Appendix C. Pre PAIR Acceptance Report

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MOBILEPOWER
SOLUTIONS

MPS Project #N2-373

1800 NW 169th Pl., B200
Beaverton, OR 97006
Phone 503-645-6789
Fax 503-645-8117

Lithium-Ion Pouch Cell Pre- Hermeticity Testing

**Electrovaya, SKC, Kokam, Saehan,
Quallion and LG**


Testing Performed by:

**Mobile Power Solutions
1800 NW 169th Pl., B200
Beaverton, OR 97006**

Prepared for: NASA

1

Update, October 12, 2007

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MOBILEPOWER SOLUTIONS


MPS Project #N2-373

Scope

Eight samples of lithium-ion pouch cells from six different manufacturers were subjected to non-destructive pre-tests prior to hermeticity testing.

Tasks:

- A. Serialize
- B. Visual Inspection
- C. Weigh (+/-5mg)
- D. Dimensions (Thickness, +/-0.1mm)
- E. OCV (+/-1mV)
- F. CCV, C/2 for 10s (+/-1mV)
- G. Initial DCIR during C/2 CCV
- H. 1kHz ACZ (+/-10mOhm)
- I. 50% SoC DCIR
- J. Capacity at 3.2V during C/2 discharge

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MPS Project #N2-373

Physical Characteristics (A, B, C, D, E, H)

Equipment:

MPS #109, Sartorius CP224S Analytical Balance, 0.0001g resolution, Std.Dev. \leq 0.0001g

MPS #59, Sartorius CP324S Analytical Balance, 0.001g resolution, Std.Dev. \leq 0.0001g

MPS #097 Mitutoyo 573-282-20 Caliper, 0.01mm resolution, Accuracy 0.001mm

MPS#T144 Agilent 4338B Milliohmeter

Data collection from instruments is direct to digital file.

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MPS Project #N2-373

Physical Characteristic Results:

A. B. Serialization and Visual

Manufacturer	MPS Sample #	Manufacturer Reference	Visual Observations
Electrovaya	N2-373-E-1	Lot # 13955 / SN # 01090	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-2	n/a	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-3	Lot # 12802 / SN # 15UB-1507	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-4	Lot # 12802 / SN # 15UB-1129	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-5	*011518	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-6	FGM 62	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-7	Lot # 13955 / SN # 010519	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-8	n/a	Sticky residue (removed by MPS); Felt pen markings
			Positive Tab Loose
SKC	N2-373-SKC-9	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-10	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-11	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-12	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-13	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-14	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-15	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-16	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
LG	N2-373-LG-17	E-bike B04A24, 1070758MGC 000899A043	n/a
LG	N2-373-LG-18	E-bike A03K01 1070318LGC 000945A009	n/a
LG	N2-373-LG-19	E-bike B04A24 1070758LGC 000899A020	n/a
LG	N2-373-LG-20	E-bike B04A24 1070758LGC 000899A025	n/a
LG	N2-373-LG-21	E-bike B04A24 1070758LGC 000899A050	n/a
LG	N2-373-LG-22	E-bike B04A24 1070758LGC 000899A010	n/a
LG	N2-373-LG-23	E-bike B04A24 1070757LGC 000899A036	n/a
LG	N2-373-LG-24	E-bike B04A24 1070758LGC 000899A006	n/a
Kokam	N2-373-K-25	S 68106100 SBXPE12A00235	n/a
Kokam	N2-373-K-26	S 68106100 SBXPD03B00099	n/a
Kokam	N2-373-K-27	S 68106100 SBXPD03B00097	n/a
Kokam	N2-373-K-28	S 68106100 SBXPE12A00358	n/a
Kokam	N2-373-K-29	S 68106100 SBXPD03B00122	n/a
Kokam	N2-373-K-30	S 68106100 SBXPD03B00103	n/a
Kokam	N2-373-K-31	S 68106100 SBXPD03B00126	n/a
Kokam	N2-373-K-32	S 68106100 SBXPD03B00165	n/a
Saehan	N2-373-SA-33	n/a	Tabs are bent, but serviceable
Saehan	N2-373-SA-34	n/a	Tabs are bent, but serviceable
Saehan	N2-373-SA-35	n/a	n/a
Saehan	N2-373-SA-36	n/a	n/a
Saehan	N2-373-SA-37	n/a	n/a
Saehan	N2-373-SA-38	n/a	n/a
Saehan	N2-373-SA-39	n/a	n/a
Saehan	N2-373-SA-40	n/a	n/a
Quallion	N2-373-Q-41	X07G023 006	n/a
Quallion	N2-373-Q-42	X07G023 023	n/a
Quallion	N2-373-Q-43	X07G023 003	n/a
Quallion	N2-373-Q-44	X07G023 007	n/a
Quallion	N2-373-Q-45	X07G023 024	n/a
Quallion	N2-373-Q-46	X07G023 004	n/a
Quallion	N2-373-Q-47	X07G023 005	n/a
Quallion	N2-373-Q-48	X07G023 001	n/a

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MPS Project #N2-373


C. D. E. H. Mass, OCV, Thickness Dimension, and 1kHz ACZ

Sample #	Mass (g)	Voltage (V)	Thickness (mm)	1kHz ACZ (mOhm)
N2-373-E-1	159.1727	3.69	9.51	48.85
N2-373-E-2	163.5403	0.721	8.67	32.65
N2-373-E-3	159.4332	3.381	8.94	32.77
N2-373-E-4	160.563	2.183	8.9	35.24
N2-373-E-5	162.7594	0.695	8.6	42.53
N2-373-E-6	159.1939	0.784	8.62	34.37
N2-373-E-7	161.5333	3.71	8.81	40.21
N2-373-E-8	162.5678	0.586	N/A rejected CK	N/A rejected CK
N2-373-SKC-9	62.9885	3.827	4.6	25.12
N2-373-SKC-10	62.9844	3.827	4.64	25.51
N2-373-SKC-11	62.9233	3.828	4.6	26.11
N2-373-SKC-12	62.9748	3.828	4.61	25.35
N2-373-SKC-13	63.1912	3.829	4.61	25.61
N2-373-SKC-14	63.1283	3.83	4.6	25.39
N2-373-SKC-15	63.0306	3.828	4.59	25.36
N2-373-SKC-16	62.9577	3.825	4.56	25.05
N2-373-LG-17	241.057	3.877	6.82	2.33
N2-373-LG-18	242.063	3.877	6.88	2.32
N2-373-LG-19	241.214	3.876	6.83	2.40
N2-373-LG-20	240.949	3.874	6.86	2.40
N2-373-LG-21	241.101	3.875	6.86	2.38
N2-373-LG-22	240.557	3.875	6.83	2.40
N2-373-LG-23	240.715	3.876	6.85	2.56
N2-373-LG-24	240.55	3.875	6.83	2.37
N2-373-K-25	158.5679	3.816	7.23	3.39
N2-373-K-26	159.0047	3.828	7.4	3.54
N2-373-K-27	159.4119	3.814	7.36	3.49
N2-373-K-28	158.9945	3.824	7.35	3.24
N2-373-K-29	159.189	3.816	7.35	3.34
N2-373-K-30	159.5089	3.818	7.34	3.39
N2-373-K-31	159.2459	3.817	7.41	3.44
N2-373-K-32	158.9172	3.819	7.3	3.42
N2-373-SA-33	43.1787	3.921	6.37	6.68
N2-373-SA-34	42.5146	3.915	6.33	6.84
N2-373-SA-35	43.0327	3.896	6.44	7.11
N2-373-SA-36	43.1238	3.899	6.41	6.99
N2-373-SA-37	43.0882	3.902	6.48	7.00
N2-373-SA-38	43.1122	3.913	6.41	6.68
N2-373-SA-39	43.3197	3.905	6.44	6.82
N2-373-SA-40	43.1969	3.874	6.38	6.92
N2-373-Q-41	96.1482	3.39	7.31	2.92
N2-373-Q-42	96.5907	3.389	7.28	3.06
N2-373-Q-43	96.2612	3.393	7.37	3.00
N2-373-Q-44	96.3156	3.39	7.36	2.96
N2-373-Q-45	96.1503	3.389	7.35	2.99
N2-373-Q-46	96.2459	3.39	7.34	3.07
N2-373-Q-47	96.2644	3.394	7.35	3.03
N2-373-Q-48	96.4231	3.391	7.33	2.94

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Characteristics under Load

The following data was collected on a Maccor 4000 Series automated battery cycler. A summary of the procedure follows:


- One minute of open circuit data collection
- 30 seconds of discharge at a C/25 current (pre-pulse background)
- 200mS of discharge at C/2 with high speed data acquisition for initial DCIR
- C/2 discharge continued for 10s to collect a CCV reading for the “as-received” condition
- Sample was charged at C/4 to 4.2 volts and a taper to C/25
- One hour rest step
- Sample discharged at C/4 for 120 minutes to reach 50% state of charge
- The discharge current was reduced to C/25 for one minute (pre-pulse background)
- 200mS of discharge at C/2 with high speed data acquisition for 50% DCIR
- C/4 discharge continued until 3.0V with capacity data collected at 3.2V
- Samples recharged to 50% SoC
- One hour rest

Electrovaya

The samples failed to cycle properly. The following is a table of the summary data that was collected where possible.

	E1	E2	E3	E4	E5	E6	E7	E8
InitOCV	3.685	0.688	3.377	2.181	0.679	0.774	3.706	Brkn Tab
C/25 V1	3.569	0.500	3.239	1.373	0.000	0.000	3.643	Brkn Tab
C/25	0.296	0.296	0.296	0.296	0.000	0.000	0.296	Brkn Tab
C/2 V2	3.347	0.000	3.070	1.119	0.000	0.000	3.458	Brkn Tab
C/2	3.700	0.000	3.700	3.700	0.000	0.000	3.700	Brkn Tab
CCV10s	2.946	0.000	2.369	0.500	0.000	0.000	3.206	Brkn Tab
Charge1 Ah	2.822	8.716	8.359	8.650	8.735	8.419	6.538	Brkn Tab
C/25 V3	0.000	3.627	3.675	3.691	3.636	3.629	3.570	Brkn Tab
C/25	0.000	0.296	0.296	0.296	0.296	0.296	0.296	Brkn Tab
C/2 V4	0.000	3.457	3.524	3.519	3.447	3.465	3.375	Brkn Tab
C/2	0.000	3.700	3.700	3.700	3.700	3.700	3.700	Brkn Tab
								Brkn Tab
3.2V Ah	0.000	4.716	5.991	6.146	4.868	4.710	3.785	Brkn Tab
3.0V Ah	0.000	6.284	6.881	6.925	6.547	6.291	4.653	Brkn Tab
								Brkn Tab
DCIRi	0.065	0.000	0.050	0.075	0.000	0.000	0.054	Brkn Tab
50%DCIR	0.000	0.050	0.044	0.051	0.056	0.048	0.057	Brkn Tab

Sample #1 was at 3.68V open circuit but only 2.95V after 10s at C/2. On the first charge the cell only took on 2.8Ah before tapering to less than C/25 amperes at 4.2V. The discharge step to 50% capacity was time based so >2.8Ah was removed and no further data could be collected.

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MOBILEPOWER SOLUTIONS

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Sample #2 was 0.69V at incoming. The initial pulse and the C/2 CCV steps could not run at such low voltage. The charge input 8.7Ah and stopped on a programmed time limit of 6 hours. It was still taking 370mA (C/20) when the charge was halted. The 50% DCIR and the capacity at 3.2V were collected normally. Discharge to 3.0V was only 72% of the previous charge.

Sample #3 was 3.38V initially. The initial DCIR and 10s CCV data were taken. The charge terminated on the 6 hour limit with 8.36Ah input. The discharge at 3.0V was only 83% of the charge.


Sample #4 was initially 2.18V. The minimum voltage on the C/2 DCIR was 1.12V so that data, 75mOhms, should be disregarded. The 10s CCV was not collected since the cell went below a .5V limit within 6 seconds. The cell charged for 6 hours and took on 8.65Ah. It discharged 6.9Ah at 3.0V.

Sample #5 was 0.68V at incoming. It did not pulse or run the 10s CCV. It halted charge at 6 hours with 8.4Ah. It discharged 6.55Ah. Note this cell and the others showed abnormally high capacity between 3.2V and 3.0V. After discharging 4.9Ah at 3.2V, the cell delivered another 1.65Ah before reaching 3.0V. That is 22% of the cell's rated capacity.

Sample #6 had an initial voltage of 0.77V. It's performance was similar to sample 5, but it did halt charge on current taper just 22 seconds before 6 hours elapsed.

Sample #7 had a normal OCV of 3.7V. It functioned for the initial DCIR and CCV checks. The cell's charge was abnormal. It began to taper current at only 30 minutes into the C/4 charge when the voltage hit the 4.2V limit. It took on only 6.5Ah total before the 6 hours elapsed and charge was halted. It discharged only 4.65Ah total above 3.0V which is only 63% of rated capacity.

Sample #8 was discovered to have a fractured positive tab at incoming inspection. The crack was at the root of the tab near the seal. The most likely cause was the almost 180 degree fold made at this location when the cells were packed for shipment.

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SKC:

	E9	E10	E11	E12	E13	E14	E15	E16
InitOCV	3.823	3.823	3.823	3.824	3.825	3.826	3.823	3.821
C/25 V1	3.815	3.816	3.816	3.817	3.817	3.819	3.817	3.813
C/25	0.124	0.124	0.124	0.124	0.124	0.124	0.124	0.124
C/2 V2	3.760	3.762	3.760	3.760	3.761	3.763	3.762	3.755
C/2	1.550	1.550	1.550	1.550	1.550	1.550	1.550	1.550
CCV10s	3.747	3.748	3.747	3.747	3.748	3.750	3.749	3.742
Charge1 Ah	1.555	1.558	1.555	1.557	1.558	1.560	1.553	1.555
C/25 V3	3.777	3.777	3.777	3.778	3.777	3.778	3.778	3.778
C/25	0.124	0.124	0.124	0.124	0.124	0.124	0.124	0.124
C/2 V4	3.725	3.727	3.725	3.725	3.724	3.726	3.726	3.724
C/2	1.550	1.550	1.550	1.550	1.550	1.550	1.550	1.550
3.2V Ah	3.245	3.244	3.245	3.249	3.253	3.259	3.247	3.243
3.0V Ah	3.286	3.285	3.286	3.290	3.294	3.299	3.287	3.284
DCIRi	0.039	0.038	0.040	0.039	0.039	0.040	0.039	0.041
50%DCIR	0.036	0.035	0.037	0.037	0.037	0.037	0.036	0.038

Kokam:

	K9	K10	K11	K12	K13	K14	K15	K16
InitOCV	3.813	3.825	3.811	3.823	3.812	3.815	3.814	3.817
C/20 V1	3.808	3.820	3.806	3.818	3.808	3.810	3.809	3.812
C/20	0.320	0.320	0.320	0.320	0.320	0.320	0.320	0.320
C/2 V2	3.768	3.779	3.765	3.778	3.767	3.769	3.768	3.770
C/2	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
CCV10s	3.761	3.772	3.758	3.771	3.760	3.762	3.761	3.763
Charge1 Ah	3.399	3.199	3.437	3.252	3.370	3.347	3.381	3.309
C/20 V3	3.768	3.764	3.766	3.767	3.765	3.766	3.766	3.765
C/20	0.320	0.320	0.320	0.320	0.320	0.320	0.320	0.320
C/2 V4	3.733	3.729	3.731	3.733	3.730	3.730	3.731	3.729
C/2	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
3.2V Ah	8.123	8.028	8.116	8.110	8.055	8.091	8.122	8.051
3.0V Ah	8.324	8.232	8.322	8.310	8.260	8.296	8.328	8.256
DCIRi	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011
50%DCIR	0.009	0.010	0.010	0.009	0.009	0.010	0.010	0.010

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Saehan:

	SA9	SA10	SA11	SA12	SA13	SA14	SA15	SA16
InitOCV	3.917	3.911	3.892	3.895	3.898	3.909	3.901	3.870
C/25 V1	3.914	3.908	3.888	3.891	3.894	3.905	3.898	3.867
C/25	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084
C/2 V2	3.892	3.886	3.867	3.869	3.873	3.884	3.877	3.846
C/2	1.050	1.050	1.050	1.050	1.050	1.050	1.050	1.050
CCV10s	3.881	3.875	3.856	3.859	3.862	3.873	3.866	3.837
Charge1 Ah	0.713	0.727	0.770	0.771	0.764	0.740	0.774	0.826
C/25 V3	3.807	3.806	3.805	3.806	3.806	3.806	3.808	3.808
C/25	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084
C/2 V4	3.788	3.787	3.786	3.787	3.787	3.788	3.790	3.790
C/2	1.050	1.050	1.050	1.050	1.050	1.050	1.050	1.050
3.2V Ah	2.118	2.092	2.083	2.091	2.083	2.092	2.118	2.109
3.0V Ah	2.137	2.113	2.100	2.109	2.106	2.111	2.139	2.131
DCIRi	0.022	0.023	0.022	0.022	0.022	0.022	0.022	0.021
50%DCIR	0.020	0.020	0.019	0.019	0.020	0.019	0.019	0.019

Quallion:

	Q9	Q10	Q11	Q12	Q13	Q14	Q15	Q16
InitOCV	3.384	3.384	3.386	3.383	3.381	3.384	3.388	3.386
C/25 V1	3.380	3.379	3.382	3.379	3.377	3.380	3.384	3.381
C/25	0.126	0.126	0.126	0.126	0.126	0.126	0.126	0.126
C/2 V2	3.368	3.367	3.370	3.367	3.364	3.368	3.372	3.369
C/2	1.575	1.575	1.575	1.575	1.575	1.575	1.575	1.575
CCV10s	3.352	3.351	3.354	3.351	3.349	3.352	3.356	3.353
Charge1 Ah	3.321	3.322	3.306	3.324	3.335	3.316	3.317	3.326
C/25 V3	3.971	3.973	3.970	3.971	3.970	3.971	3.971	3.972
C/25	0.126	0.126	0.126	0.126	0.126	0.126	0.126	0.126
C/2 V4	3.964	3.965	3.962	3.963	3.963	3.964	3.963	3.965
C/2	1.575	1.575	1.575	1.575	1.575	1.575	1.575	1.575
3.2V Ah	3.329	3.328	3.316	3.331	3.345	3.322	3.327	3.334
3.0V Ah	3.405	3.405	3.392	3.408	3.422	3.398	3.403	3.411
DCIRi	0.008	0.008	0.008	0.008	0.009	0.008	0.008	0.008
50%DCIR	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005

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LG:

	LG9	LG10	LG11	LG12	LG13	LG14	LG15	LG16
InitOCV	3.874	3.874	3.873	3.871	3.872	3.872	3.873	3.871
C/25 V1	3.869	3.870	3.868	3.867	3.868	3.867	3.868	3.867
C/25	0.400	0.400	0.400	0.400	0.400	0.400	0.400	0.400
C/2 V2	3.841	3.842	3.841	3.838	3.839	3.839	3.839	3.838
C/2	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
CCV10s	3.828	3.830	3.827	3.825	3.827	3.826	3.826	3.825
Charge1 Ah	4.861	4.775	4.864	4.909	4.890	4.889	4.867	4.900
C/25 V3	3.848	3.843	3.847	3.848	3.848	3.847	3.847	3.847
C/25	0.400	0.400	0.400	0.400	0.400	0.400	0.400	0.400
C/2 V4	3.824	3.819	3.823	3.823	3.823	3.823	3.821	3.822
C/2	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
3.2V Ah	9.347	9.144	9.314	9.338	9.338	9.311	9.328	9.315
3.0V Ah	9.462	9.256	9.429	9.454	9.454	9.426	9.443	9.430
DCIRI	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006
50%DCIR	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005

Closing Summary:

Four ElectroVaya samples were received with almost no voltage. One sample was received with a fractured positive tab and could not be cycled. Attempts to perform the Acceptance Test Cycles on the cells were only partially successful.


A CD containing softcopy versions of all data, both processed and raw, will be delivered to the address specified in the order.

End of Test Report

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Appendix D. PAIR Leak Rate Report

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TPTR 2008-0001

Lithium Ion Pouch Cell PA-IR Hermeticity Testing NASA/Johnson Space Center NNJ08HA51P


John Baker, Don Nolte, Scott Angerman, Pinakin Shah, Barbara Stachowiak

January 2008

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FORWARD

Teledyne Energy Systems was contracted by NASA/Johnson Space Center, under order number NNJ08HA51P, to qualitatively determine the leak rates of various lithium ion pouch cells using Photo Acoustic Infrared (PA-IR) analysis. This work was conducted to determine the suitability of this test method for determining the leak rate of pouch cells. The lithium ion pouch cell designs were evaluated for NASA spacesuit and spacewalking tools. The high specific energy and energy densities of the designs make them attractive for use, however, the designs must be compatible with long duration vacuum environments. Results of the PA-IR testing at room ambient and temperature extremes (-40 °C and 54 °C) are given in this report.


Approved by:



Charles W.
Sparks Facility Manager

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INTRODUCTION

Lithium ion pouch cells were received from NASA/JSC via Mobile Power Solutions of Beaverton, Oregon, where the cells were electrically tested. The Statement of Work (included as Appendix A) required testing six cells from six different manufacturers for hermeticity, using photo acoustic-infrared (PA-IR) spectroscopy.


For the PA-IR analysis, a gas sample was pumped into the analysis chamber where that gas was excited using a specific frequency of IR light. The frequency of IR light was determined by an optical filter, which was selected based on solvents which may have been in the cells. The tuned frequency of IR light had a wavelength from 7.5 μm to 8.5 μm . This particular frequency caused excitation of the covalent carbonate functional group $[\text{O}=\text{C}(\text{O}-\text{R})_2]$ in chemicals containing that functional group. It should be noted that some sulfur containing compounds are also excited in the same wavelength region. The excitation generated an acoustical signal, which was converted to an electrical signal using very sensitive microphones. The electrical signal was directly proportional to concentration. Diethyl ester carbonic acid (diethyl carbonate, DEC) $[\text{O}=\text{C}(\text{C}_2\text{H}_5\text{O})_2]$ was used as the calibration standard.

Cells analyzed by this method were stored for a period of time at a specified temperature or temperature profile in an aluminized heat-sealed bag. Gases escaping the cell were sampled from the aluminized heat-sealed bag and analyzed. Any gaseous compound containing covalent carbonate (DEC, PC, EC, EMC, DMC, MPC, etc.) was detected and provided a signal which read as a concentration based on the DEC standard.


Cells were received from Electrovaya (E), SKC (SKC), LG (LG), Kokam (K), Saehan (SA), and Quallion (Q). An initial open-circuit potential, mass, and visual observations were recorded for each cell. Three randomly selected cells from each manufacturer were stored at 24 °C for 24 days in aluminized-heat seal bags. Three randomly selected cells from each manufacturer were stored in aluminized-heat seal bags while undergoing a prescribed set of thermal cycles between -40 °C and 54 °C.

Following storage or thermal cycling, the aluminized-heat seal bags containing the cells were evaluated for DEC content using a Brüel & Kjær Multi-gas Monitor Type 1302 (now Innova 1412 manufactured by LumaSense Technologies). The analyzed values were converted to a leak rate of milligrams/month (mg/mo).

The results showed that the leak rates were higher with cells that were thermal cycled between -40 °C and 54 °C than cells that were stored at 24 °C. Additionally the results indicated that Manufacturer E cells demonstrated greater leakage rates than other manufacturer's cells. The details of the analysis are contained in this report.

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PROCEDURES


Equipment

Digital Multi-meter:	Agilent model 34401A Serial number US36136278 Calibration due 5/23/2008
Balance:	Sartorius model TE3135 Serial number 21350307 Calibration due 4/30/2008
Calipers:	Mitutoyo model CD-6" C5 Serial number 0235500 Calibration due 4/27/2008
Data Acquisition Unit:	Agilent model 34970A Serial number MY41002580 Calibration due 6/26/2008
Room Temperature Monitor:	Maccor Series 4000 Battery Cycler Serial number A010702 Calibrate as needed
Temperature Calibrator:	Model CL23A Serial number 016708 Calibration due 5/24/2008
Environmental Chamber:	Tenny Model T115-1.5 with Versa Tenn V controller Serial number 28256-01 Calibrate as needed
Gas Analyzer:	Brüel & Kjær Multi-gas Monitor Type 1302 (B&K 1302) Serial number 1684154 Calibrate as needed

Incoming Inspection

Cells were removed from their shipping containers. The cells were stored in a dryroom with a minimum dewpoint of -40 °C for a minimum of one day prior to making any measurements. Water vapor interferes with the gas analysis, therefore all work was conducted in a dryroom to minimize water exposure.

The mass of each cell was recorded to the nearest mg. The potential of each cell was recorded to the nearest 10 µV (when possible). Visual observations were recorded for each cell. Representative photographs were taken for each manufacturer's cells. External

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dimensions were recorded for a representative cell from each manufacturer to calculate to volume of each manufacturer's cells.

Aluminized Heat-Seal Bag Production

Aluminized heat-seal bags were produced from Class PPD laminated packaging material (polyester/polyethylene/aluminum foil/Surlyn®). One bag was produced for each cell to be tested plus additional bags to serve as blank specimens or spares. A single sheet (225 mm x 580 mm) of PPD material was cut, then folded perpendicular to the long edge to form a rectangular bag. The bag was heat sealed along the two long sides. At the bottom end of the bag, the two corners were compressed and sealed about an inch from the corner to form a flat bottom. The final open-end bag is shown in Figure 1. The internal volume of each aluminized heat-seal bag was approximately 1,254 mL.



Figure 1. Aluminized Heat-Seal Bag


The aluminized heat-sealed bags are used to accumulate escaping gases from each cell for analysis. Aluminized heat-sealed bags were produced in a dryroom environment to minimize water vapor content.

Temperature Storage/Cycling

Cell identification numbers were sorted, randomly, into two groups. One group was designated as the 24 °C storage group and the other was designated as the temperature cycling group. Three cells from each manufacturer were designated for each group.

Each cell was placed inside an aluminized heat-sealed bag. The open end of the bag was heat sealed closed in a dryroom atmosphere.

Cells in aluminized heat-sealed bags designated for the 24 °C storage group were placed in a 24 °C ± 3 °C temperature controlled environment for 24 days. The room temperature was monitored with a Type-T thermocouple connected to a Maccor series 4000 battery cycler input channel, which was calibrated using a thermocouple calibrator. At the end of the

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storage period, the aluminized heat-sealed bags containing the cells were moved to a dryroom and stored for a minimum of 2 hours prior to analysis.

Cells designated for the temperature cycling group were placed in aluminized heat-sealed bags just prior to temperature cycling. The aluminized heat-sealed bags were placed in a programmable environmental chamber. The temperature inside the environmental chamber was monitored with a Type-T thermocouple connected to an Agilent 34970A data acquisition unit. The thermocouple input was calibrated with a thermocouple calibrator.

The environmental chamber was programmed to change from room ambient to $-40\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ at a rate of $1.5\text{ }^{\circ}\text{C} \pm 1.0\text{ }^{\circ}\text{C}/\text{mn}$. The dwell time at $-40\text{ }^{\circ}\text{C}$ was set for $3\text{ h} \pm 0.1\text{ h}$. Following dwell, the chamber changed to $54\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ at a rate of $1.5\text{ }^{\circ}\text{C} \pm 1.0\text{ }^{\circ}\text{C}/\text{mn}$. The chamber was programmed to dwell at $54\text{ }^{\circ}\text{C}$ for $3\text{ h} \pm 0.1\text{ h}$. Following the dwell period the chamber changed temperature to $-40\text{ }^{\circ}\text{C}$. The environmental chamber was programmed for a total of 24 hot and 24 cold dwell periods. Following the last hot dwell period, the environmental chamber was programmed to return to $24\text{ }^{\circ}\text{C}$ at a rate of $1.5\text{ }^{\circ}\text{C} \pm 1.0\text{ }^{\circ}\text{C}/\text{mn}$.

At the end of the storage period, the aluminized heat-sealed bags containing the cells were moved to the dryroom and stored for a minimum of 2 hours prior to analysis.


Analysis

The B&K 1302 PA-IR analyzer was located in a dryroom with a dewpoint of at least $-40\text{ }^{\circ}\text{C}$. The instrument was calibrated with zero grade air (Roberts Oxygen Lot 01001011204) and a $201\text{ }\mu\text{g/g}$ DEC in air (Scott Specialty Gas Lot CAL015767) prepared calibration standard. Verification of the calibration using a $2.10\text{ }\mu\text{g/g}$ DEC in air (Scott Specialty Gas Lot CLM003749) prepared calibration standard yielded a result of $2.34\text{ }\mu\text{g/g}$ DEC in air; approximately 11% error at the low end of the calibration. Significant calibration standard did not remain after the calibration to verify the results at the upper end of the calibration curve.


The instrument was connected to a Teflon[®] tube attached to a needle. The needle was pushed through the flat bottom of the aluminized heat-sealed bags containing cells. The instrument pulled a sample of air into the analysis chamber and analyzed the sample for DEC content based on the calibration standard. The instrument was allowed to sample each aluminized heat-sealed bag three times. Following the third sample, the needle was removed from the aluminized heat-sealed bag and allowed to sample dryroom air. The instrument was allowed to self-purge until the reading returned to a level equivalent to that for an aluminized heat-sealed bag containing no cell.

Post-Test Inspection

After each aluminized heat-sealed bag was sampled for DEC, the cell was removed from the bag. The mass of each cell was recorded, the potential of each cell was recorded, and visual observations were made for each cell.

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RESULTS & DISCUSSION

Temperature

Temperature was recorded during storage and during temperature cycling of cells while in aluminized heat-sealed bags. The temperature monitored for cells stored at 24 °C for 24 days is shown in Figure 2. The storage area was maintained at 24 °C +0.6/-0.4 °C during the storage period.

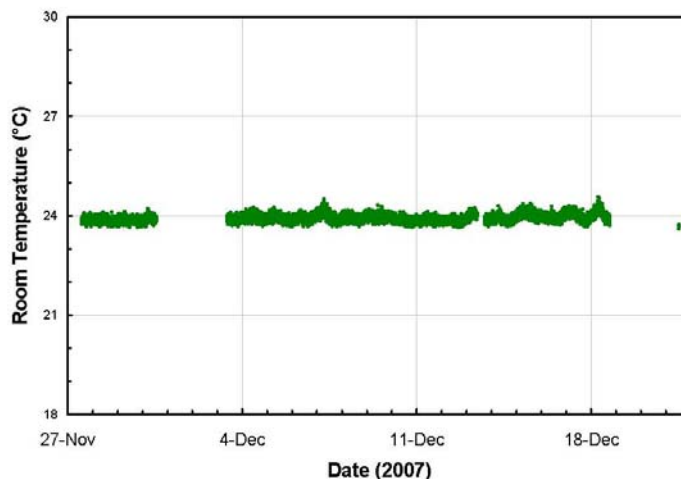


Figure 2. Area Temperature During Storage Period for 24 °C Stored Cells

The temperature recorded during the thermal cycling profile is shown in Figure 3. Heating rates were at the nominal specification level, however cooling rates were at the minimum of the specification level; limited by available equipment. An example of the ramp rates achieved is shown in Figure 4. It is clear from Figure 4 that the equipment used had a significantly slower cooling rate than heating rate. However, the rate achieved was within specification.

More than half of the 54 °C dwell times exceeded the specified time limit. It is believed that these time variations were due to the equilibration of the environmental chamber; the chamber was programmed to deliver a guaranteed soak period at a given set-point. The exact dwell times – calculated from the time at which the temperature was within 0.5 °C of the specified dwell time – recorded during testing are given in Table I. It is not believed that the time variations affected the final outcome of the results.

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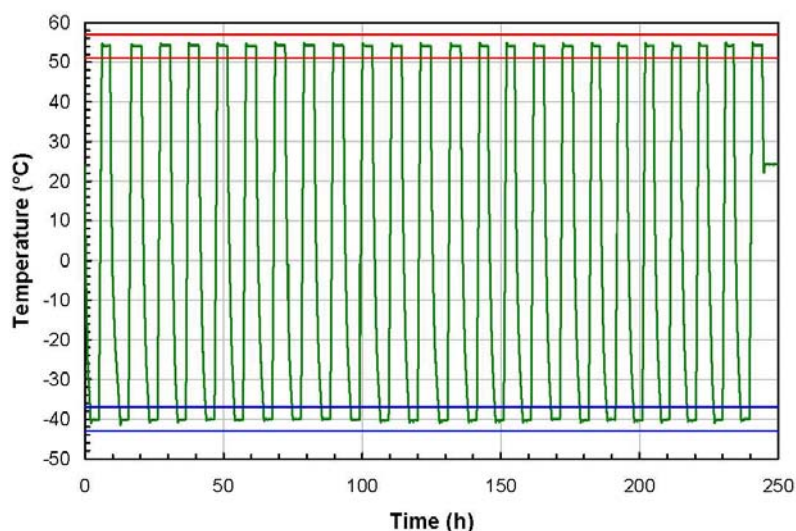


Figure 3. Recorded Temperature for Cells Cycled Between -40 °C and 54 °C

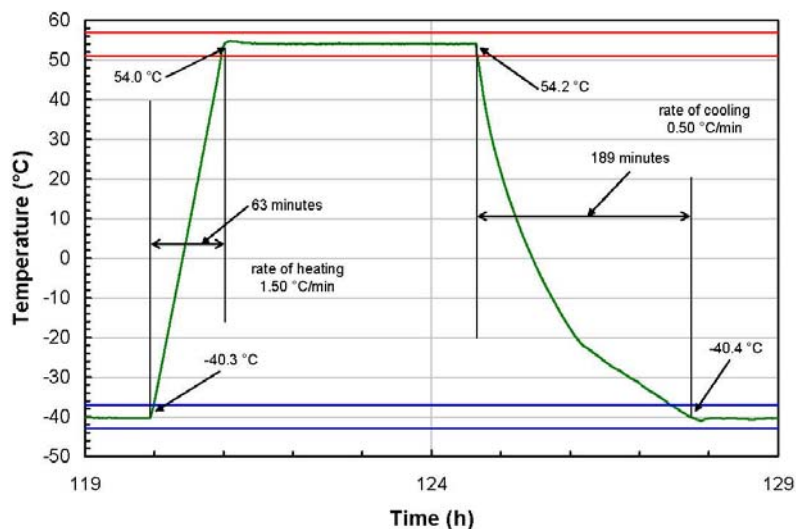



Figure 4. Ramp Rates Achieved During Temperature Cycling

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**Table I. Dwell Times for Each
Temperature Cycling Dwell Period**


Dwell	Time at -40 °C (h)	Time at 54 °C (h)
1	3.0	3.0
2	3.0	3.6
3	3.0	3.6
4	3.0	3.6
5	3.0	3.7
6	3.0	3.6
7	3.1	3.6
8	3.0	3.7
9	3.0	3.7
10	3.0	3.6
11	3.0	3.6
12	3.0	3.6
13	3.1	3.7
14	3.0	3.0
15	3.0	3.0
16	3.0	3.6
17	3.0	3.6
18	3.0	3.0
19	3.1	3.0
20	3.0	3.0
21	3.0	3.0
22	3.0	3.0
23	3.0	3.0
24	3.0	3.6

Analysis Results

Three readings, as µg/g of DEC in air, were recorded for each aluminized heat-sealed bag containing a cell. Those three readings for each sample were averaged prior to further analysis of the data. In addition to the cell samples, empty aluminized heat-sealed bags were tested for each temperature group. The empty aluminized heat-sealed bags were treated the same as those containing cells; they went through the same storage period or temperature cycling profile. Readings recorded for the empty aluminized heat-sealed bags were insignificant compared to readings for those containing cells, therefore no blank correction was made during subsequent calculations.

Three cells from each manufacturer were analyzed for each temperature group. The analysis readings are plotted in Figure 5. The values shown in Figure 5 represent the concentration of DEC inside each aluminized heat-sealed bag. The calibration of the instrument was performed with DEC. The instrument is sensitive to the covalent carbonate chemical structure, therefore, any chemical with a covalent carbonate adds to the detection during the analysis. This adds a level of uncertainty to the analysis. Care must be exercised when comparing results between manufacturers since different manufacturers use different electrolyte compositions and those compositions were unknown.

Each different type of cell had a different volume, so the volume of air inside the aluminized heat-sealed bags was different from manufacturer to manufacturer. To compare results between manufacturers the actual volume of air, and therefore the mass, must be accounted

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for in the analysis. To compare differences between 24 °C stored cells and temperature cycled cells, the time difference must be accounted for in the analysis.

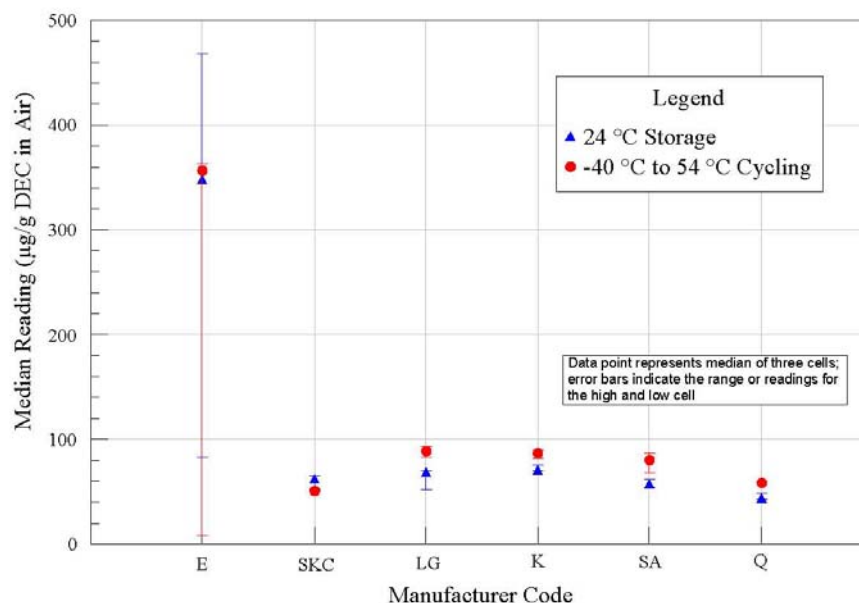


Figure 5. PA-IR Analysis Readings for 24 °C Stored Cells and -40 °C to 54 °C Temperature Cycled Cells

For a given reading, a correction based on the volume of air inside the aluminized heat-sealed bag was made. The volume of air was converted to mass using the density of air. For the purposes of this analysis the density of dry air ($1.2845 \times 10^{-3} \text{ g/mL}^1$) at 20.5 °C and 760 mm Hg was used. The equation for converting to mass of equivalent DEC from µg/g DEC in Air is given by Equation 1.

$$M = R \times (V_{\text{bag}} - V_{\text{cell}}) \times (1.2845 \times 10^{-3} \text{ g/mL}) \quad (1)$$

where,

M is mass of equivalent DEC in µg


R is the analysis reading in µg/g

V_{bag} is the volume of the bag

V_{cell} is the volume of the cell

The value M represents the total mass of DEC inside an aluminized heat-sealed bag; more appropriately the description was given as equivalent DEC since the analysis product can not be identified as DEC but compared to a calibration based on DEC.

¹ *CRC Handbook of Chemistry and Physics*, CRC Press: Boca Raton, FL, 1982.

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To compare all results, values of M must be corrected for storage or temperature cycling time since these times vary. Equation 2 shows the correction for time which yields a leak rate as equivalent mg/mo (a month being 30 days) DEC.

$$L = M \times \frac{1\text{mg}}{1000\mu\text{g}} \times \frac{1}{S} \times \frac{30\text{dy}}{1\text{mo}} \quad (2)$$

where,
 L is leak rate in equivalent $\mu\text{g}/\text{mo}$ DEC
 M is mass of equivalent DEC in μg
 S is storage or temperature cycling duration in dy

The median leak rate results with range error bars are given in Figure 6. The data suggests that all cells leak more when cycled between -40°C and 54°C than when stored at 24°C . However, all cells have some leakage even at room temperature. Additionally, the data suggests that Manufacturer E cells have a higher rate of leakage than other manufacturer's cells. The data also suggests that Manufacturer E's cells have a higher variability of leakage.

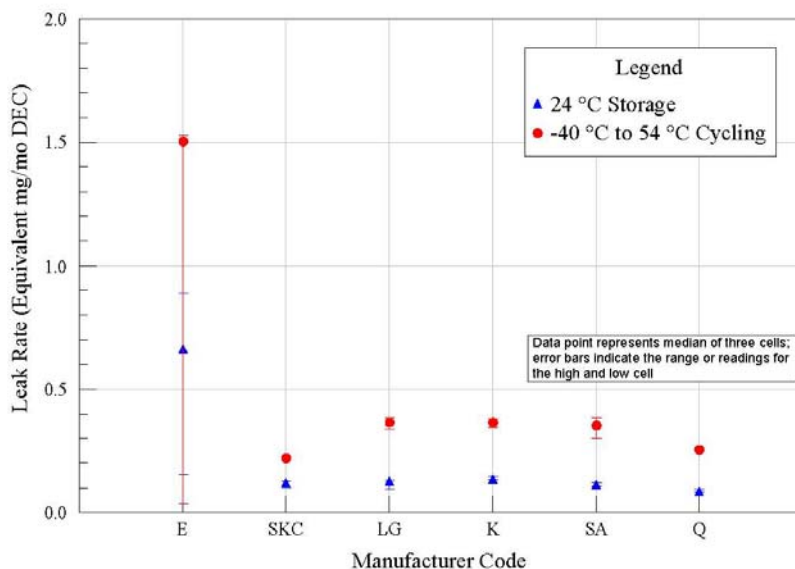


Figure 6. Leak Rate for Manufacturer's Cells during 24 °C Storage and -40 °C to 54 °C Temperature Cycling

As part of the analysis, the mass of each cell was recorded before and after testing. A mass change was calculated and normalized with time to produce a mass change rate; similar to leak rate. The mass change rate is plotted in Figure 7. Although the actual measured mass change rate differs in magnitude significantly from the equivalent DEC leak rate, the pattern is similar. These similarities help validate the equivalent DEC leak rate data. Like the leak

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rate data the mass change rate data indicates that all cells leak more when cycled between -40 °C and 54 °C than when stored at 24 °C. The data also suggests that Manufacturer E cells have a higher rate of leakage than other manufacturer's cells. The data also suggests that Manufacturer E's cells have a higher variability of leakage.

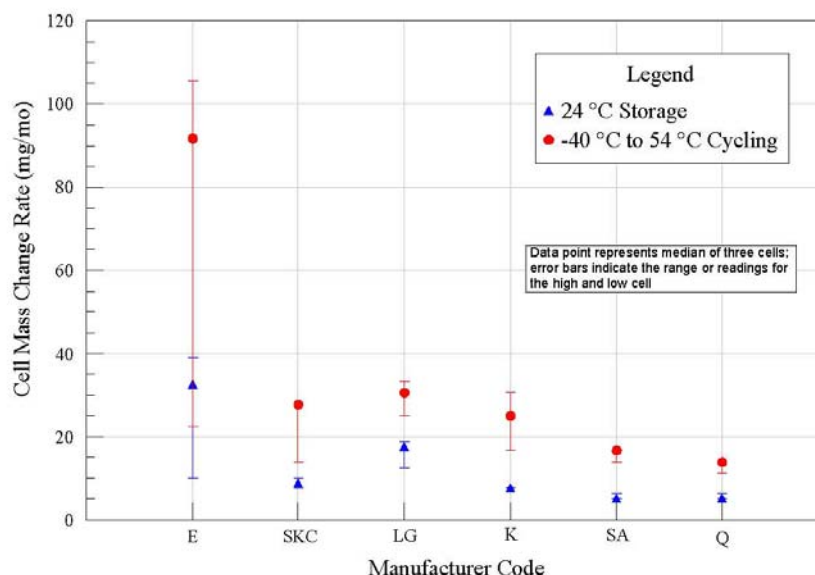


Figure 7. Mass Change for Manufacturer's Cells during 24 °C Storage and -40 °C to 54 °C Temperature Cycling

The data collected for each cell is shown in Table II. In addition to the data presented and discussed, the potential change data should be noted. In general, the potential drop during testing was higher in cells that had been temperature cycled than for those stored at 24 °C. One exception was with Manufacturer E cells where the variation was very large. The second exception was with Manufacturer LG cells where the potential change difference may be negligible.

Generally, potential drop is indicative of the self-discharge properties of cells. The Manufacturer Q cells had significantly higher potential drops than cells from other manufacturers.

Visual Inspection

There were no visual changes noted for any cells after the storage or temperature cycling period. General observations for each manufacturer's cells are noted below.

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Table II. Analysis Data


Sample	Manufacturer	Storage*	Pre-Storage Mass (g)	Post-Storage Mass (g)	Mass Change (mg)	Pre-Storage Potential (V)	Post-Storage Potential (V)	Potential Change (mV)	Reading 1 (µg/g DEC)	Reading 2 (µg/g DEC)	Reading 3 (µg/g DEC)	Average (µg/g DEC)	Median Leak Rate (mg/mo DEC)
N2-373-E-7	Electrolysa	N	161 492			3 95528							
N2-373-E-8	Electrolysa	N	162 511			broken tab							
N2-373-E-9	Electrolysa	R	159 116	159 085	-31	0 4654	0 944	-21.4	467	469	469	468	0.663
N2-373-E-4	Electrolysa	R	160 531	160 523	-8	3 85736	3 85268	-4.68	81	82	83	82	
N2-373-E-6	Electrolysa	R	159 134	159 108	-26	3 87483	3 87174	-3.09	344	349	353	348	
N2-373-E-2	Electrolysa	T	163 465	163 427	-38	3 87500	3 86503	-9.97	8	8	9	8	1.505
N2-373-E-3	Electrolysa	T	159 406	159 398	-8	3 85412	3 83902	-15.1	352	356	362	357	
N2-373-E-5	Electrolysa	T	162 692	162 659	-33	3 86229	3 85602	-6.27	359	364	366	363	
N2-373-SKC-9	SKC	N	62 973			3 79011							
N2-373-SKC-10	SKC	N	62 967			3 79014							
N2-373-SKC-11	SKC	R	62 906	62 900	-6	3 79010	3 78759	-2.51	60	63	63	62	0.123
N2-373-SKC-12	SKC	R	62 950	62 950	-0	3 79000	3 78764	-2.36	65	65	64	65	
N2-373-SKC-16	SKC	R	62 941	62 934	-7	3 79011	3 78767	-2.44	50	51	53	51	
N2-373-SKC-13	SKC	T	63 174	63 169	-5	3 78996	3 78495	-4.91	49	51	51	50	0.221
N2-373-SKC-14	SKC	T	63 112	63 102	-10	3 78994	3 78488	-5.06	50	51	51	50	
N2-373-SKC-15	SKC	T	63 013	63 003	-10	3 78996	3 78504	-4.92	52	53	53	52	
N2-373-LG-19	LG	N	241 178			3 88888							
N2-373-LG-23	LG	N	240 668			3 88053							
N2-373-LG-18	LG	R	242 029	242 019	-10	3 89250	3 88999	-2.51	51	53	51	51	0.127
N2-373-LG-21	LG	R	241 061	241 046	-15	3 88818	3 88632	-1.86	68	70	71	70	
N2-373-LG-34	LG	R	240 507	240 493	-14	3 88877	3 88775	-1.02	67	69	70	69	
N2-373-LG-17	LG	T	241 018	241 010	-8	3 88804	3 88679	-1.26	82	83	82	82	0.366
N2-373-LG-20	LG	T	240 809	240 898	-11	3 88827	3 88672	-1.55	92	93	94	93	
N2-373-LG-22	LG	T	240 516	240 504	-12	3 88876	3 88758	-1.18	88	89	90	89	
N2-373-K-25	Kokam	N	158 541			3 78876							
N2-373-K-31	Kokam	N	159 218			3 78669							
N2-373-K-28	Kokam	R	158 966	158 960	-6	3 78899	3 78674	-2.25	69	71	72	71	0.135
N2-373-K-29	Kokam	R	159 160	159 154	-6	3 78897	3 78664	-2.33	74	76	76	75	
N2-373-K-30	Kokam	R	159 480	159 474	-6	3 78875	3 78654	-2.21	69	70	71	70	
N2-373-K-26	Kokam	T	158 976	158 967	-9	3 78924	3 78540	-3.84	85	87	88	86	0.367
N2-373-K-27	Kokam	T	159 385	159 374	-11	3 78874	3 78503	-3.71	88	90	90	90	
N2-373-K-32	Kokam	T	158 889	158 883	-6	3 78881	3 78508	-3.73	81	82	83	82	
N2-373-SA-38	Saehan	N	43 101			3 85170							
N2-373-SA-40	Saehan	N	43 187			3 81309							
N2-373-SA-33	Saehan	R	43 170	43 165	-5	3 81561	3 81054	-5.07	56	58	58	57	0.114
N2-373-SA-37	Saehan	R	43 077	43 073	-4	3 81593	3 81279	-3.14	60	61	62	61	
N2-373-SA-39	Saehan	R	43 309	43 305	-4	3 81349	3 81034	-3.15	53	54	54	54	
N2-373-SA-34	Saehan	T	42 504	42 499	-5	3 81563	3 81045	-5.18	86	87	88	87	0.354
N2-373-SA-35	Saehan	T	43 023	43 017	-6	3 81636	3 81153	-4.85	65	69	70	68	
N2-373-SA-36	Saehan	T	43 113	43 107	-6	3 81593	3 81102	-4.81	80	81	80	80	
N2-373-Q-45	Qualiton	N	96 130			3 93655							
N2-373-Q-46	Qualiton	N	96 226			3 93871							
N2-373-Q-42	Qualiton	R	96 570	96 565	-5	3 93809	3 93456	-3.53	43	43	43	43	0.085
N2-373-Q-43	Qualiton	R	96 240	96 236	-4	3 93871	3 93730	-1.41	48	48	48	48	
N2-373-Q-47	Qualiton	R	96 244	96 240	-4	3 93837	3 93736	-1.01	43	44	44	44	
N2-373-Q-41	Qualiton	T	96 128	96 123	-5	3 93788	3 93594	-3.04	59	57	58	58	0.254
N2-373-Q-44	Qualiton	T	96 294	96 290	-4	3 93800	3 93781	-0.27	58	59	59	59	
N2-373-Q-48	Qualiton	T	96 492	96 497	5	3 93810	3 93658	-1.52	59	60	60	60	
EMPTY BAG-A		R							0.23	0.26	0.28	0.25	
EMPTY BAG-B		T							0.21	0.24	0.28	0.24	
EMPTY BAG-C		T							0.28	0.24	0.25	0.25	
DRYROOM AIR		R							0.07	0.07	0.07	0.07	

* (T) temperature profile, (R) 24 °C, (N) not tested

For Manufacturer E cells, the visual observations noted indicate that the cells appeared to be leaking with whitish solidified materials on the cell exterior, and the cells were generally visually unappealing. A representative cell is pictured in Figure 8. Figure 9 shows a magnified view of a corner on one of the Manufacturer E cells; solidified whitish material is visible. It was noted that Cell 8 had a broken tab; potential readings could not be made.

A few small dimples and scrapes were noted for the Manufacturer SKC cells, but in general there were few visual observations noted. A representative cell is pictured in Figure 10.

Notes of wrinkled sections of bags were noted for the Manufacturer LG cells. However as with the Manufacturer SKC cells, few visual observations were noted. A representative cell is pictured in Figure 11.

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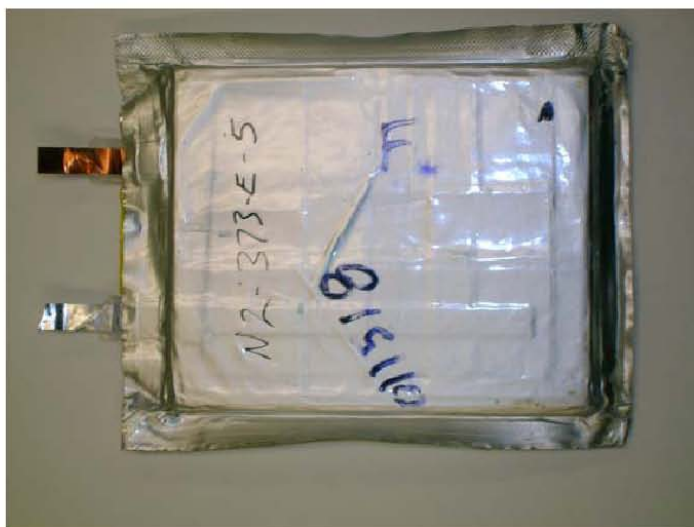



Figure 8. Manufacturer E Cell



Figure 9. Corner of Manufacturer E Cell Showing Whitish Solid Deposits

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Notations concerning the Manufacturer K cells indicated that the electrodes appeared bumpy through the bag material. There were also some notes of scrapes on the bags. A representative cell for Manufacturer K is shown in Figure 12; the bumpy appearance of the electrodes is visible.

Visual observations for Manufacturer SA cells included notes of wrinkled areas of bag material. A representative cell is pictured in Figure 13.

Few visual notations were made for Manufacturer Q cells and included notes of slight scrapes and dings on the bags. A representative Manufacturer Q cell is shown in Figure 14.

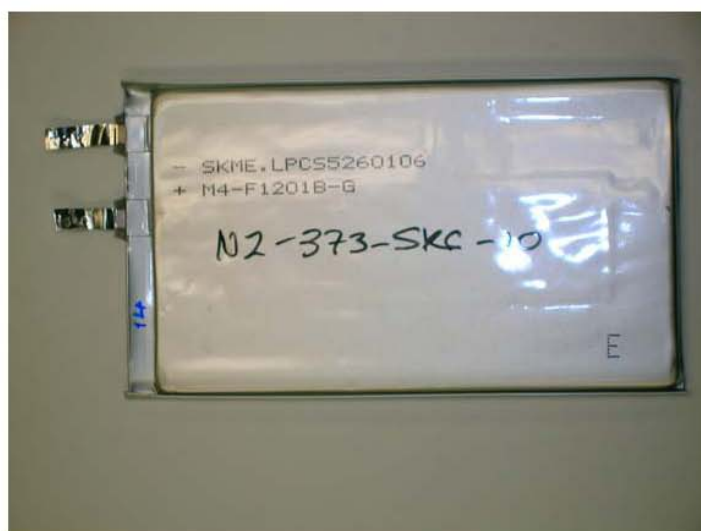



Figure 10. Manufacturer SKC Cell

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Figure 11. Manufacturer LG Cell



Figure 12. Manufacturer K Cell

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Figure 13. Manufacturer SA Cell



Figure 14. Manufacturer Q Cell

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CONCLUSIONS


Lithium ion pouch cells were received from NASA/JSC via Mobile Power Solutions of Beaverton, Oregon, where the cells were electrically tested. Cells were stored for a period of time at a specified temperature or temperature profile in aluminized heat-sealed bags. Gases escaping the cells were accumulated then sampled and analyzed using a Brüel & Kjær Multi-gas Monitor Type 1302; uses the PA-IR analysis technique.

Cells were received from Electrovaya (E), SKC (SKC), LG (LG), Kokam (K), Saehan (SA), and Quallion (Q). The results showed that the leak rates were higher with cells that were thermally cycled between -40 °C and 54 °C than for cells that were stored at 24 °C. Additionally, the results indicate that Manufacturer E cells demonstrated higher leakage rates and more variability of leakage rate than other manufacturer's cells. The results of the PA-IR analysis were verified by actual mass change measurements.

The cells were returned to Mobile Power Solutions following analysis.

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APPENDIX A – STATEMENT OF WORK

Lithium Ion Pouch Cell Hermeticity Testing Statement of Work Rev B

- 1.0 Scope – This effort involves receiving samples from 6 different lithium ion pouch cells from NASA, subject them to acceptance tests, thermal cycling testing and determining each cell's hermeticity with a photo acoustic infrared leak detection method.
- 2.0 Purpose – The objectives of the effort to qualitatively determine which pouch cells designs achieve the highest hermeticity for assessing the suitability of these designs for space (vacuum) applications. A secondary objective is to get experience with the merits of the PA-IR leak test method.
- 3.0 Background – Pouch cell designs are sought for NASA spacesuit and spacewalking tools due to their high specific energy and energy density. However, hermeticity limitations are undetermined and may not be compliant with long duration vacuum environments.
- 4.0 Test Cells – NASA will provide a minimum of 6 pouch cells from each manufacturer. The six manufacturers will mostly likely be SKC, Kokam, Saehan, LTC, ElectroVaya, and LG. All the cell designs shall be in the 3 to 10Ah range.
- 5.0 Acceptance Tests – The contractor shall perform the following tests; visual, mass (± 5 mg), and OCV (± 1 mV).
- 6.0 Thermal Cycling – The contractor shall place each cell in individual seal containers. Expose half the cells from each manufacturer to the following regime: Starting at ambient temperature, ramp down to -40 ± 3 °C, when chamber controlling temperature sensor placed on a cell gets within range, dwell 3 ± 0.1 hours, then ramp up to 54 ± 3 °C, when same sensor gets within range, dwell 3 ± 0.1 hours, then repeat for a total of 24 hot and 24 cold dwells. Maintain ramp rates within 1.5 ± 1.0 °C/min. For post-test check-out, perform visual inspection, record mass to ± 1 mg, and measure OCVs of each cell.
- 7.0 PA-IR Leak Test – After the thermal cycles are complete and the room temperature cells have spent over 2 weeks in their containers, the contractor shall test the hermeticity of each cell from each manufacturer (6) using the photo acoustic infrared method described in John Baker's 2005 NASA Battery Workshop.
- 8.0 Cell Return – The contractor shall return the cells to NASA-JSC for post test acceptance testing.
- 9.0 Reporting – The contractor shall generate a test report with a description of the test methods and all test results.
- 10.0 Timing – The contractor shall delivery the test report within 2 months after receipt of order and 1.5 months after receipt of the cells.


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Appendix E. Post PAIR Acceptance Report

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MPS Project #N2-373-2 (Post-Hermeticity Test)

MOBILE-POWER

SOLUTIONS


1800 NW 169th Pl., B200
Beaverton, OR 97006
Phone 503-645-6789
Fax 503-645-8117

Lithium-Ion Pouch Cell Post- Hermeticity Testing

**Electrovaya, SKC, Kokam, Saehan,
Quallion and LG**

Testing Performed by:

**Mobile Power Solutions
1800 NW 169th Pl., B200
Beaverton, OR 97006**

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MOBILEPOWER SOLUTIONS

MPS Project #N2-373-2 (Post-Hermeticity Test)

Scope

Eight samples of lithium-ion pouch cells from six different manufacturers were subjected to non-destructive pre-tests after hermeticity testing.

Tasks:

- A. Serialize (Done in Pre-Test Only)
- B. Visual Inspection (Done in Pre-Test Only)
- C. Weigh (+/-5mg)
- D. Dimensions (Thickness, +/-1mm)
- E. OCV (+/-1mV)
- F. CCV, C/2 for 10s (+/-1mV)
- G. Initial DCIR during C/2 CCV
- H. 1kHz ACZ (+/-10mOhm)
- I. 50% SoC DCIR
- J. Capacity at 3.2V during C/2 discharge

Incoming Characteristics (A, B, C, D, E, H)

Equipment:


MPS #109, Sartorius CP224S Analytical Balance, 0.0001g resolution, Std.Dev. ≤ 0.0001g

MPS #59, Sartorius CP324S Analytical Balance, 0.001g resolution, Std.Dev. ≤ 0.0001g

MPS #097 Mitutoyo 573-282-20 Caliper, 0.01mm resolution, Accuracy 0.001mm

MPS#T144 Agilent 4338B Milliohmeter

Data collection from instruments is direct to digital file.

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MPS Project #N2-373-2 (Post-Hermeticity Test)

Incoming Characteristic Results:

Tasks A. Serialization and B. Visual Inspection

Manufacturer	MPS Sample #	Manufacturer Reference	Visual Observations
Electrovaya	N2-373-E-1	Lot # 13955 / SN # 01090	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-2	n/a	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-3	Lot # 12802 / SN # 15UB-1507	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-4	Lot # 12802 / SN # 15UB-1129	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-5	*011518	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-6	FGM 62	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-7	Lot # 13955 / SN # 010519	Sticky residue (removed by MPS); Felt pen markings
Electrovaya	N2-373-E-8	n/a	Sticky residue (removed by MPS); Felt pen markings
			Positive Tab Loose
SKC	N2-373-SKC-9	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-10	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-11	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-12	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-13	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-14	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-15	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
SKC	N2-373-SKC-16	M4-F1201B-G	Shipping damage, tabs are bent, but serviceable
LG	N2-373-LG-17	E-bike B04A24, 1070758MGC 000899A043	n/a
LG	N2-373-LG-18	E-bike A03K01 1070318LGC 000945A009	n/a
LG	N2-373-LG-19	E-bike B04A24 1070758LGC 000899A020	n/a
LG	N2-373-LG-20	E-bike B04A24 1070758LGC 000899A025	n/a
LG	N2-373-LG-21	E-bike B04A24 1070758LGC 000899A050	n/a
LG	N2-373-LG-22	E-bike B04A24 1070758LGC 000899A010	n/a
LG	N2-373-LG-23	E-bike B04A24 1070757LGC 000899A036	n/a
LG	N2-373-LG-24	E-bike B04A24 1070758LGC 000899A006	n/a
Kokam	N2-373-K-25	S 68106100 SBXPE12A00235	n/a
Kokam	N2-373-K-26	S 68106100 SBXPD03B00099	n/a
Kokam	N2-373-K-27	S 68106100 SBXPD03B00097	n/a
Kokam	N2-373-K-28	S 68106100 SBXPE12A00358	n/a
Kokam	N2-373-K-29	S 68106100 SBXPD03B00122	n/a
Kokam	N2-373-K-30	S 68106100 SBXPD03B00103	n/a
Kokam	N2-373-K-31	S 68106100 SBXPD03B00126	n/a
Kokam	N2-373-K-32	S 68106100 SBXPD03B00165	n/a
Saehan	N2-373-SA-33	n/a	Tab are bent, but serviceable
Saehan	N2-373-SA-34	n/a	Tab are bent, but serviceable
Saehan	N2-373-SA-35	n/a	n/a
Saehan	N2-373-SA-36	n/a	n/a
Saehan	N2-373-SA-37	n/a	n/a
Saehan	N2-373-SA-38	n/a	n/a
Saehan	N2-373-SA-39	n/a	n/a
Saehan	N2-373-SA-40	n/a	n/a
Quallion	N2-373-Q-41	X07G023 006	n/a
Quallion	N2-373-Q-42	X07G023 023	n/a
Quallion	N2-373-Q-43	X07G023 003	n/a
Quallion	N2-373-Q-44	X07G023 007	n/a
Quallion	N2-373-Q-45	X07G023 024	n/a
Quallion	N2-373-Q-46	X07G023 004	n/a
Quallion	N2-373-Q-47	X07G023 005	n/a
Quallion	N2-373-Q-48	X07G023 001	n/a

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MOBILEPOWER SOLUTIONS

MPS Project #N2-373-2 (Post-Hermeticity Test)

Tasks C. Pre- and Post-Mass and E. Pre- and Post-OCV

Sample #	Pre-Mass (g)	Post-Mass (g)	Pre-Voltage (V)	Post-Voltage (V)
N2-373-E-1	159.17	159.08	3.690	1.233
N2-373-E-2	163.54	163.43	0.721	3.867
N2-373-E-3	159.43	159.41	3.381	3.834
N2-373-E-4	160.56	160.54	2.183	3.846
N2-373-E-5	162.76	162.66	0.695	3.854
N2-373-E-6	159.19	159.10	0.784	3.869
N2-373-E-7	161.53	161.48	3.710	3.954
N2-373-E-8	162.57	N/A rejected CK	0.586	N/A rejected CK
N2-373-SKC-9	62.99	62.97	3.827	3.786
N2-373-SKC-10	62.98	62.97	3.827	3.786
N2-373-SKC-11	62.92	62.90	3.828	3.786
N2-373-SKC-12	62.97	62.95	3.828	3.786
N2-373-SKC-13	63.19	63.17	3.829	3.783
N2-373-SKC-14	63.13	63.10	3.830	3.783
N2-373-SKC-15	63.03	63.01	3.828	3.783
N2-373-SKC-16	62.96	62.94	3.825	3.786
N2-373-LG-17	241.06	241.03	3.877	3.884
N2-373-LG-18	242.06	242.03	3.877	3.888
N2-373-LG-19	241.21	241.19	3.876	3.886
N2-373-LG-20	240.95	240.92	3.874	3.884
N2-373-LG-21	241.10	241.08	3.875	3.885
N2-373-LG-22	240.56	240.52	3.875	3.884
N2-373-LG-23	240.72	240.68	3.876	3.886
N2-373-LG-24	240.55	240.52	3.875	3.885
N2-373-K-25	158.57	158.54	3.816	3.785
N2-373-K-26	159.00	158.98	3.828	3.784
N2-373-K-27	159.41	159.39	3.814	3.783
N2-373-K-28	158.99	158.97	3.824	3.785
N2-373-K-29	159.19	159.16	3.816	3.785
N2-373-K-30	159.51	159.49	3.818	3.785
N2-373-K-31	159.25	159.22	3.817	3.785
N2-373-K-32	158.92	158.89	3.819	3.783
N2-373-SA-33	43.18	43.16	3.921	3.808
N2-373-SA-34	42.51	42.50	3.915	3.806
N2-373-SA-35	43.03	43.02	3.896	3.807
N2-373-SA-36	43.12	43.10	3.899	3.806
N2-373-SA-37	43.09	43.08	3.902	3.810
N2-373-SA-38	43.11	43.10	3.913	3.810
N2-373-SA-39	43.32	43.31	3.905	3.807
N2-373-SA-40	43.20	43.18	3.874	3.806
N2-373-Q-41	96.15	96.13	3.390	3.884
N2-373-Q-42	96.59	96.57	3.389	3.906
N2-373-Q-43	96.26	96.24	3.393	3.913
N2-373-Q-44	96.32	96.30	3.390	3.886
N2-373-Q-45	96.15	96.14	3.389	3.913
N2-373-Q-46	96.25	96.23	3.390	3.917
N2-373-Q-47	96.26	96.25	3.394	3.914
N2-373-Q-48	96.42	96.40	3.391	3.885

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MPS Project #N2-373-2 (Post-Hermeticity Test)


Tasks D. Pre- and Post-Thickness Dimension and H. Pre- and Post-1 kHz ACZ

Sample #	Pre-Thickness (mm)	Post-Thickness (mm)	Pre-1kHz ACZ (mOhm)	Post-1kHz ACZ (mOhm)
N2-373-E-1	9.51	9.45	48.85	58.50
N2-373-E-2	8.67	9.08	32.65	38.90
N2-373-E-3	8.94	8.90	32.77	34.30
N2-373-E-4	8.90	8.77	35.24	39.14
N2-373-E-5	8.60	8.82	42.53	44.10
N2-373-E-6	8.62	8.80	34.37	38.54
N2-373-E-7	8.81	9.02	40.21	37.21
N2-373-E-8	N/A rejected CK	N/A rejected CK	N/A rejected CK	N/A rejected CK
N2-373-SKC-9	4.60	4.60	25.12	25.26
N2-373-SKC-10	4.64	4.60	25.51	25.45
N2-373-SKC-11	4.60	4.61	26.11	25.05
N2-373-SKC-12	4.61	4.61	25.35	25.65
N2-373-SKC-13	4.61	4.63	25.61	25.85
N2-373-SKC-14	4.60	4.61	25.39	25.41
N2-373-SKC-15	4.59	4.60	25.36	25.59
N2-373-SKC-16	4.56	4.59	25.05	25.14
N2-373-LG-17	6.82	6.87	2.33	2.64
N2-373-LG-18	6.88	6.92	2.32	2.61
N2-373-LG-19	6.83	6.85	2.40	2.64
N2-373-LG-20	6.86	6.86	2.40	2.73
N2-373-LG-21	6.86	6.85	2.38	2.65
N2-373-LG-22	6.83	6.88	2.40	2.78
N2-373-LG-23	6.85	6.86	2.56	2.81
N2-373-LG-24	6.83	6.85	2.37	2.66
N2-373-K-25	7.23	7.27	3.39	3.52
N2-373-K-26	7.40	7.41	3.54	3.79
N2-373-K-27	7.36	7.37	3.49	3.88
N2-373-K-28	7.35	7.27	3.24	3.55
N2-373-K-29	7.35	7.38	3.34	3.68
N2-373-K-30	7.34	7.33	3.39	3.67
N2-373-K-31	7.41	7.36	3.44	3.61
N2-373-K-32	7.30	7.31	3.42	3.64
N2-373-SA-33	6.37	6.37	6.68	6.97
N2-373-SA-34	6.33	6.32	6.84	7.29
N2-373-SA-35	6.44	6.47	7.11	7.61
N2-373-SA-36	6.41	6.41	6.99	7.35
N2-373-SA-37	6.48	6.42	7.00	7.51
N2-373-SA-38	6.41	6.32	6.68	7.12
N2-373-SA-39	6.44	6.47	6.82	7.24
N2-373-SA-40	6.38	6.37	6.92	6.97
N2-373-Q-41	7.31	7.45	2.92	3.55
N2-373-Q-42	7.28	7.37	3.06	3.52
N2-373-Q-43	7.37	7.45	3.00	3.31
N2-373-Q-44	7.36	7.47	2.96	3.63
N2-373-Q-45	7.35	7.45	2.99	3.27
N2-373-Q-46	7.34	7.42	3.07	3.40
N2-373-Q-47	7.35	7.44	3.03	3.67
N2-373-Q-48	7.33	7.46	2.94	3.65

Prepared for: NASA

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February 18, 2008

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MPS Project #N2-373-2 (Post-Hermeticity Test)

Characteristics under Load

The following data was collected on a Maccor 4000 Series automated battery cycler. A summary of the procedure follows:


- One minute of open circuit data collection
- 30 seconds of discharge at a C/25 current (pre-pulse background)
- 200mS of discharge at C/2 with high speed data acquisition for initial DCIR
- C/2 discharge continued for 10s to collect a CCV reading for the “as-received” condition
- Sample was charged at C/4 to 4.2 volts and a taper to C/25
- One hour rest step
- Sample discharged at C/4 for 120 minutes to reach 50% state of charge
- The discharge current was reduced to C/25 for one minute (pre-pulse background)
- 200mS of discharge at C/2 with high speed data acquisition for 50% DCIR
- C/4 discharge continued until 3.0V with capacity data collected at 3.2V
- Samples recharged to 50% SoC
- One hour rest

Electrovaya (Pre-Test):

The samples failed to cycle properly. The following is a table of the summary data that was collected where possible.

	E1	E2	E3	E4	E5	E6	E7	E8
InitOCV	3.685	0.688	3.377	2.181	0.679	0.774	3.706	Brkn Tab
C/25 V1	3.569	0.500	3.239	1.373	0.000	0.000	3.643	Brkn Tab
C/25	0.296	0.296	0.296	0.296	0.000	0.000	0.296	Brkn Tab
C/2 V2	3.347	0.000	3.070	1.119	0.000	0.000	3.458	Brkn Tab
C/2	3.700	0.000	3.700	3.700	0.000	0.000	3.700	Brkn Tab
CCV10s	2.946	0.000	2.369	0.500	0.000	0.000	3.206	Brkn Tab
Charge1 Ah	2.822	8.716	8.359	8.650	8.735	8.419	6.538	Brkn Tab
C/25 V3	0.000	3.627	3.675	3.691	3.636	3.629	3.570	Brkn Tab
C/25	0.000	0.296	0.296	0.296	0.296	0.296	0.296	Brkn Tab
C/2 V4	0.000	3.457	3.524	3.519	3.447	3.465	3.375	Brkn Tab
C/2	0.000	3.700	3.700	3.700	3.700	3.700	3.700	Brkn Tab
								Brkn Tab
3.2V Ah	0.000	4.716	5.991	6.146	4.868	4.710	3.785	Brkn Tab
3.0V Ah	0.000	6.284	6.881	6.925	6.547	6.291	4.653	Brkn Tab
								Brkn Tab
DCIRI	0.065	0.000	0.050	0.075	0.000	0.000	0.054	Brkn Tab
50%DCIR	0.000	0.050	0.044	0.051	0.056	0.048	0.057	Brkn Tab

Sample #1 was at 3.68V open circuit but only 2.95V after 10s at C/2. On the first charge the cell only took on 2.8Ah before tapering to less than C/25 amperes at 4.2V. The discharge step to 50% capacity was time based so >2.8Ah was removed and no further data could be collected.

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MPS Project #N2-373-2 (Post-Hermeticity Test)

Sample #2 was 0.69V at incoming. The initial pulse and the C/2 CCV steps could not run at such low voltage. The charge input 8.7Ah and stopped on a programmed time limit of 6 hours. It was still taking 370mA (C/20) when the charge was halted. The 50% DCIR and the capacity at 3.2V were collected normally. Discharge to 3.0V was only 72% of the previous charge.

Sample #3 was 3.38V initially. The initial DCIR and 10s CCV data were taken. The charge terminated on the 6 hour limit with 8.36Ah input. The discharge at 3.0V was only 83% of the charge.


Sample #4 was initially 2.18V. The minimum voltage on the C/2 DCIR was 1.12V so that data, 75mOhms, should be disregarded. The 10s CCV was not collected since the cell went below a .5V limit within 6 seconds. The cell charged for 6 hours and took on 8.65Ah. It discharged 6.9Ah at 3.0V.

Sample #5 was 0.68V at incoming. It did not pulse or run the 10s CCV. It halted charge at 6 hours with 8.4Ah. It discharged 6.55Ah. Note this cell and the others showed abnormally high capacity between 3.2V and 3.0V. After discharging 4.9Ah at 3.2V, the cell delivered another 1.65Ah before reaching 3.0V. That is 22% of the cell's rated capacity.

Sample #6 had an initial voltage of 0.77V. Its performance was similar to sample 5, but it did halt charge on current taper just 22 seconds before 6 hours elapsed.

Sample #7 had a normal OCV of 3.7V. It functioned for the initial DCIR and CCV checks. The cell's charge was abnormal. It began to taper current at only 30 minutes into the C/4 charge when the voltage hit the 4.2V limit. It took on only 6.5Ah total before the 6 hours elapsed and charge was halted. It discharged only 4.65Ah total above 3.0V which is only 63% of rated capacity.

Sample #8 was discovered to have a fractured positive tab at incoming inspection. The crack was at the root of the tab near the seal. The most likely cause was the almost 180 degree fold made at this location when the cells were packed for shipment.

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MPS Project #N2-373-2 (Post-Hermeticity Test)

Electrovaya (Post-Test):

	E1	E2	E3	E4	E5	E6	E7	E8
InitOCV	0.955	3.866	3.834	3.843	3.853	3.954	3.867	Brkn Tab
C/25 V1	0.000	3.798	3.800	3.816	3.778	3.921	3.802	Brkn Tab
C/25	0.000	0.296	0.296	0.296	0.296	0.296	0.296	Brkn Tab
C/2 V2	0.000	3.615	3.639	3.634	3.575	3.749	3.627	Brkn Tab
C/2	0.000	3.700	3.700	3.700	3.700	3.700	3.700	Brkn Tab
CCV10s	0.000	3.844	3.830	3.841	3.827	3.950	3.847	Brkn Tab
Charge1 Ah	3.738	2.998	3.414	3.620	3.098	1.702	2.858	Brkn Tab
C/25 V3	0.000	3.576	3.659	3.678	3.554	3.555	3.581	Brkn Tab
C/25	0.296	0.296	0.296	0.296	0.296	0.296	0.296	Brkn Tab
C/2 V4	0.000	3.392	3.492	3.492	3.342	3.354	3.400	Brkn Tab
C/2	3.700	3.700	3.700	3.700	3.700	3.700	3.700	Brkn Tab
								Brkn Tab
3.2V Ah	0.000	3.788	5.326	5.476	3.720	3.755	3.846	Brkn Tab
3.0V Ah	0.000	5.465	6.389	6.262	4.849	4.345	5.369	Brkn Tab
								Brkn Tab
DCIRI	0.000	0.054	0.047	0.054	0.060	0.051	0.052	Brkn Tab
50%DCIR	0.000	0.054	0.049	0.055	0.062	0.059	0.053	Brkn Tab

Sample #1 was at 0.95V open circuit and could not sustain a 30 second discharge at C/25 before reaching 0.5V at 9.86 seconds. The high rate C/2 could not be done. On the first charge the cell only took on 3.73Ah in 6 hours with a final current of 0.338A at 4.2V. The discharge step to 50% capacity was time based (120 minutes at C/4) but the cell went to 0V after 34.7 minutes. No further data could be collected.

Samples #2 to #7 had a wide variance in charge capacities. The final discharge capacities also had a wide variance and did not meet the rated capacity of 7.4Ah. The 50% DOD DCIR values did not change appreciably from the original pre-test values, but the values are higher than the other manufacturers.

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MPS Project #N2-373-2 (Post-Hermeticity Test)

SKC (Pre-Test):

	SKC9	SKC10	SKC11	SKC12	SKC13	SKC14	SKC15	SKC16
InitOCV	3.823	3.823	3.823	3.824	3.825	3.826	3.823	3.821
C/25 V1	3.815	3.816	3.816	3.817	3.817	3.819	3.817	3.813
C/25	0.124	0.124	0.124	0.124	0.124	0.124	0.124	0.124
C/2 V2	3.760	3.762	3.760	3.760	3.761	3.763	3.762	3.755
C/2	1.550	1.550	1.550	1.550	1.550	1.550	1.550	1.550
CCV10s	3.747	3.748	3.747	3.747	3.748	3.750	3.749	3.742
Charge1 Ah	1.555	1.558	1.555	1.557	1.558	1.560	1.553	1.555
C/25 V3	3.777	3.777	3.777	3.778	3.777	3.778	3.778	3.778
C/25	0.124	0.124	0.124	0.124	0.124	0.124	0.124	0.124
C/2 V4	3.725	3.727	3.725	3.725	3.724	3.726	3.726	3.724
C/2	1.550	1.550	1.550	1.550	1.550	1.550	1.550	1.550
3.2V Ah	3.245	3.244	3.245	3.249	3.253	3.259	3.247	3.243
3.0V Ah	3.286	3.285	3.286	3.290	3.294	3.299	3.287	3.284
DCIRi	0.039	0.038	0.040	0.039	0.039	0.040	0.039	0.041
50%DCIR	0.036	0.035	0.037	0.037	0.037	0.037	0.036	0.038

SKC (Post-Test):

	SKC9	SKC10	SKC11	SKC12	SKC13	SKC14	SKC15	SKC16
InitOCV	3.784	3.786	3.784	3.785	3.782	3.782	3.782	3.784
C/25 V1	3.778	3.779	3.778	3.778	3.776	3.776	3.776	3.778
C/25	0.124	0.124	0.124	0.124	0.124	0.124	0.124	0.124
C/2 V2	3.724	3.725	3.724	3.724	3.723	3.721	3.724	3.727
C/2	1.550	1.550	1.550	1.550	1.550	1.550	1.550	1.550
CCV10s	3.783	3.784	3.782	3.783	3.781	3.780	3.781	3.783
Charge1 Ah	1.743	1.740	1.743	1.744	1.753	1.764	1.750	1.740
C/25 V3	3.777	3.778	3.777	3.777	3.777	3.778	3.778	3.778
C/25	0.124	0.124	0.124	0.124	0.124	0.124	0.124	0.124
C/2 V4	3.726	3.726	3.726	3.727	3.728	3.727	3.728	3.729
C/2	1.550	1.550	1.550	1.550	1.550	1.550	1.550	1.550
3.2V Ah	3.235	3.232	3.234	3.234	3.233	3.245	3.231	3.231
3.0V Ah	3.276	3.272	3.274	3.274	3.274	3.285	3.272	3.271
DCIRi	0.037	0.038	0.038	0.038	0.037	0.038	0.037	0.036
50%DCIR	0.035	0.036	0.036	0.035	0.035	0.036	0.035	0.034

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MPS Project #N2-373-2 (Post-Hermeticity Test)

Kokam (Pre-Test):

	K9	K10	K11	K12	K13	K14	K15	K16
InitOCV	3.813	3.825	3.811	3.823	3.812	3.815	3.814	3.817
C/20 V1	3.808	3.820	3.806	3.818	3.808	3.810	3.809	3.812
C/20	0.320	0.320	0.320	0.320	0.320	0.320	0.320	0.320
C/2 V2	3.768	3.779	3.765	3.778	3.767	3.769	3.768	3.770
C/2	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
CCV10s	3.761	3.772	3.758	3.771	3.760	3.762	3.761	3.763
Charge1 Ah	3.399	3.199	3.437	3.252	3.370	3.347	3.381	3.309
C/20 V3	3.768	3.764	3.766	3.767	3.765	3.766	3.766	3.765
C/20	0.320	0.320	0.320	0.320	0.320	0.320	0.320	0.320
C/2 V4	3.733	3.729	3.731	3.733	3.730	3.730	3.731	3.729
C/2	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
3.2V Ah	8.123	8.028	8.116	8.110	8.055	8.091	8.122	8.051
3.0V Ah	8.324	8.232	8.322	8.310	8.260	8.296	8.328	8.256
DCIRi	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011
50%DCIR	0.009	0.010	0.010	0.009	0.009	0.010	0.010	0.010

Kokam (Post-Test):

	K25	K26	K27	K28	K29	K30	K31	K32
InitOCV	3.784	3.782	3.781	3.784	3.784	3.785	3.784	3.782
C/20 V1	3.779	3.777	3.776	3.779	3.779	3.780	3.780	3.777
C/20	0.320	0.320	0.320	0.320	0.320	0.320	0.320	0.320
C/2 V2	3.738	3.737	3.734	3.741	3.740	3.740	3.739	3.738
C/2	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
CCV10s	3.782	3.781	3.780	3.783	3.783	3.784	3.784	3.781
Charge1 Ah	4.366	4.293	4.366	4.344	4.302	4.342	4.356	4.310
C/20 V3	3.767	3.764	3.765	3.767	3.765	3.767	3.766	3.764
C/20	0.320	0.320	0.320	0.320	0.320	0.320	0.320	0.320
C/2 V4	3.731	3.729	3.728	3.733	3.731	3.732	3.731	3.729
C/2	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
3.2V Ah	8.077	7.962	8.020	8.053	8.020	8.053	8.069	7.964
3.0V Ah	8.278	8.164	8.223	8.252	8.221	8.255	8.272	8.165
DCIRi	0.011	0.011	0.011	0.010	0.011	0.011	0.011	0.011
50%DCIR	0.010	0.010	0.010	0.009	0.009	0.010	0.009	0.010

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MPS Project #N2-373-2 (Post-Hermeticity Test)

Saehan (Pre-Test):

	SA9	SA10	SA11	SA12	SA13	SA14	SA15	SA16
InitOCV	3.917	3.911	3.892	3.895	3.898	3.909	3.901	3.870
C/25 V1	3.914	3.908	3.888	3.891	3.894	3.905	3.898	3.867
C/25	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084
C/2 V2	3.892	3.886	3.867	3.869	3.873	3.884	3.877	3.846
C/2	1.050	1.050	1.050	1.050	1.050	1.050	1.050	1.050
CCV10s	3.881	3.875	3.856	3.859	3.862	3.873	3.866	3.837
Charge1 Ah	0.713	0.727	0.770	0.771	0.764	0.740	0.774	0.826
C/25 V3	3.807	3.806	3.805	3.806	3.806	3.806	3.808	3.808
C/25	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084
C/2 V4	3.788	3.787	3.786	3.787	3.787	3.788	3.790	3.790
C/2	1.050	1.050	1.050	1.050	1.050	1.050	1.050	1.050
3.2V Ah	2.118	2.092	2.083	2.091	2.083	2.092	2.118	2.109
3.0V Ah	2.137	2.113	2.100	2.109	2.106	2.111	2.139	2.131
DCIRi	0.022	0.023	0.022	0.022	0.022	0.022	0.022	0.021
50%DCIR	0.020	0.020	0.019	0.019	0.020	0.019	0.019	0.019

Saehan (Post-Test):

	SA33	SA34	SA35	SA36	SA37	SA38	SA39	SA40
InitOCV	3.808	3.806	3.808	3.806	3.809	3.809	3.807	3.806
C/25 V1	3.805	3.803	3.804	3.803	3.806	3.804	3.803	3.802
C/25	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084
C/2 V2	3.785	3.780	3.782	3.781	3.784	3.766	3.780	3.779
C/2	1.050	1.050	1.050	1.050	1.050	1.050	1.050	1.050
CCV10s	3.778	3.805	3.806	3.805	3.809	3.808	3.806	3.805
Charge1 Ah	1.146	1.113	1.100	1.112	1.088	1.096	1.127	1.128
C/25 V3	3.809	3.806	3.805	3.806	3.805	3.805	3.808	3.807
C/25	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084
C/2 V4	3.792	3.787	3.786	3.787	3.786	3.780	3.790	3.788
C/2	1.050	1.050	1.050	1.050	1.050	1.050	1.050	1.050
3.2V Ah	2.129	2.090	2.071	2.085	2.080	2.093	2.120	2.113
3.0V Ah	2.148	2.108	2.090	2.104	2.099	2.112	2.139	2.131
DCIRi	0.021	0.024	0.023	0.023	0.023	0.039	0.024	0.024
50%DCIR	0.018	0.020	0.020	0.019	0.020	0.026	0.019	0.020

Cell #1 had a charger failure on its first run and was repeated. Its data shows that it has a slightly higher capacity and a slightly lower DCIR than the rest of the group.

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MPS Project #N2-373-2 (Post-Hermeticity Test)

Quallion (Pre-Test):

	Q9	Q10	Q11	Q12	Q13	Q14	Q15	Q16
InitOCV	3.384	3.384	3.386	3.383	3.381	3.384	3.388	3.386
C/25 V1	3.380	3.379	3.382	3.379	3.377	3.380	3.384	3.381
C/25	0.126	0.126	0.126	0.126	0.126	0.126	0.126	0.126
C/2 V2	3.368	3.367	3.370	3.367	3.364	3.368	3.372	3.369
C/2	1.575	1.575	1.575	1.575	1.575	1.575	1.575	1.575
CCV10s	3.352	3.351	3.354	3.351	3.349	3.352	3.356	3.353
Charge1 Ah	3.321	3.322	3.306	3.324	3.335	3.316	3.317	3.326
C/25 V3	3.971	3.973	3.970	3.971	3.970	3.971	3.971	3.972
C/25	0.126	0.126	0.126	0.126	0.126	0.126	0.126	0.126
C/2 V4	3.964	3.965	3.962	3.963	3.963	3.964	3.963	3.965
C/2	1.575	1.575	1.575	1.575	1.575	1.575	1.575	1.575
3.2V Ah	3.329	3.328	3.316	3.331	3.345	3.322	3.327	3.334
3.0V Ah	3.405	3.405	3.392	3.408	3.422	3.398	3.403	3.411
DCIRI	0.008	0.008	0.008	0.008	0.009	0.008	0.008	0.008
50%DCIR	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005

Quallion (Post-Test):

	Q41	Q42	Q43	Q44	Q45	Q46	Q47	Q48
InitOCV	3.881	3.904	3.910	3.883	3.910	3.914	3.911	3.882
C/25 V1	3.879	3.902	3.908	3.881	3.909	3.912	3.909	3.880
C/25	0.126	0.126	0.126	0.126	0.126	0.126	0.126	0.126
C/2 V2	3.870	3.893	3.900	3.871	3.899	3.903	3.900	3.870
C/2	1.575	1.575	1.575	1.575	1.575	1.575	1.575	1.575
CCV10s	3.880	3.903	3.909	3.882	3.910	3.913	3.910	3.880
Charge1 Ah	2.185	2.142	2.102	2.177	2.117	2.086	2.106	2.181
C/25 V3	3.968	3.970	3.969	3.968	3.969	3.969	3.969	3.967
C/25	0.126	0.126	0.126	0.126	0.126	0.126	0.126	0.126
C/2 V4	3.959	3.962	3.961	3.959	3.961	3.961	3.960	3.959
C/2	1.575	1.575	1.575	1.575	1.575	1.575	1.575	1.575
3.2V Ah	3.046	3.127	3.139	3.052	3.158	3.147	3.140	3.047
3.0V Ah	3.125	3.207	3.217	3.131	3.237	3.226	3.219	3.126
DCIRI	0.006	0.006	0.006	0.007	0.007	0.006	0.006	0.007
50%DCIR	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006

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MPS Project #N2-373-2 (Post-Hermeticity Test)

LG (Pre-Test):

	LG9	LG10	LG11	LG12	LG13	LG14	LG15	LG16
InitOCV	3.874	3.874	3.873	3.871	3.872	3.872	3.873	3.871
C/25 V1	3.869	3.870	3.868	3.867	3.868	3.867	3.868	3.867
C/25	0.400	0.400	0.400	0.400	0.400	0.400	0.400	0.400
C/2 V2	3.841	3.842	3.841	3.838	3.839	3.839	3.839	3.838
C/2	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
CCV10s	3.828	3.830	3.827	3.825	3.827	3.826	3.826	3.825
Charge1 Ah	4.861	4.775	4.864	4.909	4.890	4.889	4.867	4.900
C/25 V3	3.848	3.843	3.847	3.848	3.848	3.847	3.847	3.847
C/25	0.400	0.400	0.400	0.400	0.400	0.400	0.400	0.400
C/2 V4	3.824	3.819	3.823	3.823	3.823	3.823	3.821	3.822
C/2	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
3.2V Ah	9.347	9.144	9.314	9.338	9.338	9.311	9.328	9.315
3.0V Ah	9.462	9.256	9.429	9.454	9.454	9.426	9.443	9.430
DCIRI	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006
50%DCIR	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005

LG (Post-Test):

	LG17	LG18	LG19	LG20	LG21	LG22	LG23	LG24
InitOCV	3.883	3.888	3.886	3.884	3.885	3.885	3.886	3.886
C/25 V1	3.880	3.884	3.881	3.879	3.881	3.880	3.881	3.881
C/25	0.400	0.400	0.400	0.400	0.400	0.400	0.400	0.400
C/2 V2	3.851	3.855	3.854	3.849	3.853	3.851	3.852	3.852
C/2	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
CCV10s	3.883	3.887	3.885	3.882	3.884	3.883	3.884	3.884
Charge1 Ah	4.584	4.587	4.650	4.569	4.672	4.552	4.669	4.647
C/25 V3	3.842	3.848	3.849	3.841	3.849	3.841	3.849	3.848
C/25	0.400	0.400	0.400	0.400	0.400	0.400	0.400	0.400
C/2 V4	3.816	3.823	3.823	3.813	3.824	3.814	3.823	3.822
C/2	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
3.2V Ah	9.193	9.268	9.351	9.176	9.363	9.159	9.373	9.335
3.0V Ah	9.307	9.380	9.464	9.290	9.476	9.273	9.488	9.448
DCIRI	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006
50%DCIR	0.006	0.005	0.006	0.006	0.006	0.006	0.006	0.006

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MPS Project #N2-373-2 (Post-Hermeticity Test)

Closing Summary:


Four Electroveya samples were initially received with almost no voltage. One sample was received with a fractured positive tab and could not be cycled. Attempts to perform the Acceptance Pre-Test Cycles on the cells were only partially successful.

On receipt for the Acceptance Post-Test Cycles, Electroveya sample #1 was found to contain a short circuit and data was unable to be collected.

Saehan's first sample, identified as SA33 by MPS, had a charger failure on its first post-test. The test was repeated and the cell performed well. The cell's capacity was slightly higher and its DCIR was slightly lower than the rest of the group.

A CD containing softcopy versions of all data, both processed and raw, will be delivered to the address specified in the order. The data is also available on the MPS/NASA ftp site.

End of Test Report

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Appendix F. Aerospace Applications of Pouch Cells

Task II : Recommendations for Aerospace Applications of Pouch Cells

Problem Description, Proposed Solutions, and Risk Assessment

Problem description:

Pouch cell designs, with either liquid or gel polymer or true polymer electrolytes, offer enhanced specific energy and energy densities compared to conventional designs with metallic cell cases. Also they have better form factor and packing efficiency and thus are an attractive option for short-life missions. There is, however one shortcoming of these design, i.e., their inability to maintain hermeticity of the cell through its lifetime. This is especially the case with electrolytes have low boiling point and high vapor pressure, which cause the pouch to open. For example, the Alliant Li-gel polymer pouch cells developed for the 2001 Mars Lander application exhibited impressive specific energies of ~ 150 Wh/kg (Fig.1). They also displayed good low temperature performance capability as shown by the discharge curves at -20°C in Fig. 2. However, these cells sustained rapid capacity fade during cycling at ambient temperature after 300 cycles, (Fig. 3). This failure is accompanied by unusually high charge to discharge capacity ratio is unusually high suggesting a significant pressure build from the parasitic electrolyte oxidation.

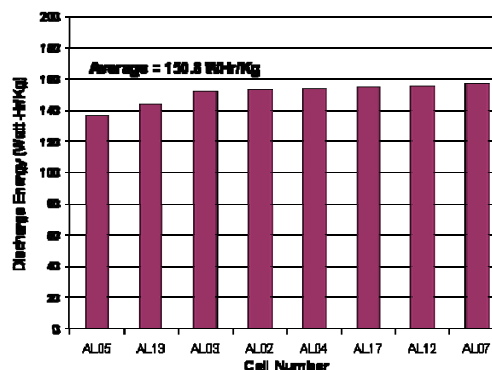


Fig. 1: Specific energy of Alliant Tech 25 Ah Li-ion gel polymer electrolyte cells at 25°C

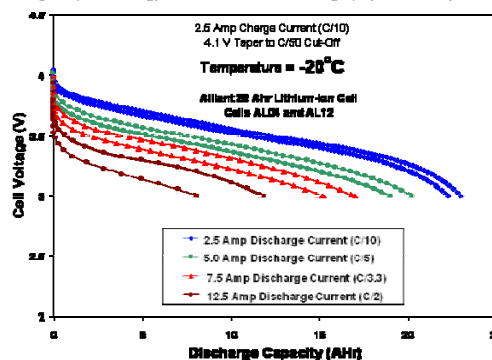


Fig. 2: Rate capability of Alliant Tech 25 Ah Li-ion gel polymer electrolyte cells at -20°C

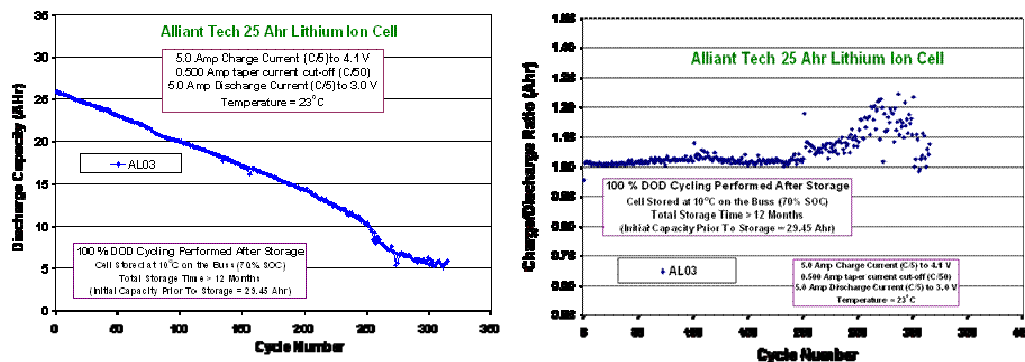


Fig. 3: Cycling of Alliant Tech 25 Ah Li-ion gel polymer electrolyte cells at ambient temperature.

It is anticipated that exposures to high temperature operations or hard vacuum would accelerate such degradation and aggravate the problem of pouch integrity. The objective of this sub-task was to evaluate performance limitations of pouch cell designs in general in space environments, specifically thermal and vacuum environments.

Proposed solution and risk assessment:


A systematic study has been undertaken to determine the viability of using pouch Li-ion and Li-ion polymer batteries under conditions relevant to space applications, specifically hard vacuum and thermal cycling. The approach adopted here was to evaluate lithium-ion pouch cells, with different electrolytes and from different manufacturers for their ability to maintain hermeticity. Furthermore, adequate screening methods were developed to identify the proper test methodology.

The test articles utilized in this study are listed in Table 2 Table 2. These include i) 4.3 Ah pouch cells made by Quallion with their baseline electrolyte, two variations of low temperature electrolytes and two variations of JPL low temperature electrolyte, ii) SKC cells with their gel polymer electrolyte, iii) Compact Power cells containing their gel polymer electrolyte as well a few of JPL low temperature electrolytes as plasticizers and iv) LTC Li-ion cells. These cells were subjected to a thorough characterization testing, which included determining the capacities as a function of charge and discharge rates at

Table 1. Various pouch cells selected for the study

Manufacturer	Type	Chemistry	
		Couple	Electrolyte
Quallion	Pouch Cells	C-Li(Mn, Ni, Co)O ₂	ED2-LT electrolyte (Quallion)
	Pouch Cells	C-Li(Mn, Ni, Co)O ₂	ED1-LT electrolyte (Quallion)
	Pouch cells	C-Li(Mn, Ni, Co)O ₂	Quallion Baseline
	Pouch cells	C-Li(Mn, Ni, Co)O ₂	Two variations of JPL Electrolytes
SKC	Pouch Cells	C-Li(CO)O ₂	Gel Polymer electrolyte (SKC)
Compact power	Pouch Cells	C-LiMn ₂ O ₄	Gel Polymer (Compact power) Also with JPL electrolytes
LTC	Pouch Cells	C-Li(Ni,Co)O ₂	Liquid Electrolyte (LTC)

different temperatures as well as determining the DC impedance of some of these as a function of state of charge and temperature. In addition, the LTC and Compact power cells have been

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well tested under 100% DOD and partial DOD cycling. These characterization tests were aimed at providing the baseline data prior to the thermal cycling and vacuum. Some of these cells were subjected to high temperature cycling, as a means of accelerating the failure that would occur over longer cycles at ambient temperature. In addition, the rest of the cells are being exposed to thermal vacuum cycling in the non-operating mode. Upon on completion of the thermal vac cycles, the cells will be once aging subjected to a detailed characterization to quantify their effects on the performance.

Data Analysis

Table 2: Values of Discharge capacity, energy and impedance of seven SKC Polymer cells at C/5 at 25°C

Characterization data

SKC Polymer Cells

As part of formation (which may have already been done by the manufacturer, seven SKC gel polymer electrolytes cells have been discharged initially at 20°C and -20°C at a nominal discharge rate of C/5. Also, in the last discharge cycle, the cell impedances were measured by DC current interrupt method. Table 2 summarizes the discharge data and the impedance values at 100%, 75% and 50% SOC. The specific energies are impressive with over 160 Wh/kg, as may be expected from the pouch cell designs. Further, the impedance (of ~25 mOhms) is comparable to cells with liquid electrolyte even with a gel polymer electrolyte. Subsequent to this formation cycling at 25°C, the cells have been conditioned also at 0 and -20°C. Tables 3 and 4 provide the summaries of these characterization data at these temperatures. As may be seen from these data, the average specific energy at 0°C is ~ 155 Wh/kg (about 98% of the room temperature value) and the average value of DC impedance is around 68 mOhms (about 2.5 times that of room temperature impedance).

Cell ID	Cell Weight (Grams)	Cell Weight (kg)	Initial Voltage	Initial Capacity (Ah)	Initial Watt-Hours	Initial Wh/kg	Calculated Impedance (mOhms) (100% SOC)	Calculated Impedance (mOhms) (75% SOC)	Calculated Impedance (mOhms) (50% SOC)
SKC01	78.56	0.0786	3.824	3.3940	12.825	163.25	27.30	30.81	36.95
SKC03	79.03	0.0790	3.826	3.3729	12.744	161.26	27.88	31.34	38.02
SKC04	78.68	0.0787	3.825	3.3783	12.764	162.22	28.08	31.18	37.24
SKC05	78.95	0.0790	3.826	3.3834	12.791	162.02	26.72	29.94	35.76
SKC06	78.67	0.0787	3.825	3.3878	12.797	162.67	29.03	32.62	38.81
SKC07	79.63	0.0796	3.820	3.3958	12.825	161.06	25.53	28.91	35.14
SKC08	79.05	0.0791	3.828	3.3873	12.821	162.19	22.52	28.83	29.82
Average	78.94	0.079	3.825	3.386	12.795	162.10	26.72	30.52	35.96

Table 3: Values of Discharge capacity, energy and Impedance of seven SKC Polymer cells at C/5 at 0°C

Cell ID	Cell Weight (kg)	Capacity at 20°C	Capacity at 0°C (RT Charge)	Watt-Hour at 0°C	Energy at 0°C (Wh/kg)	Percent of RT Capacity (%)	Calculated Impedance at 0°C (mOhms) (100% SOC)	Calculated Impedance at 0°C (mOhms) (75% SOC)	Calculated Impedance at 0°C (mOhms) (50% SOC)
SKC01	0.9786	3.3940	3.3634	3.3276	12.286	156.39	98.04	67.10	77.61
SKC03	0.9799	3.3729	3.3437	3.2196	12.226	154.70	98.15	67.02	76.15
SKC04	0.9787	3.3743	3.3515	3.3174	12.249	155.68	98.20	68.54	79.39
SKC05	0.9790	3.3834	3.3549	3.3220	12.283	155.58	98.19	65.61	76.21
SKC06	0.9787	3.3678	3.3578	3.3229	12.263	155.88	98.08	69.08	79.59
SKC07	0.9796	3.3958	3.3569	3.3398	12.338	154.94	98.35	62.77	73.45
SKC08	0.9791	3.3873	3.2827	3.2341	11.910	150.66	95.48	71.14	83.06
Average	0.9789	3.3857	3.3444	3.2196	12.222	154.83	97.78	67.32	78.21

Table 4: Values of Discharge capacity, energy and Impedance of seven SKC Polymer cells at C/5 at -20°C

Cell ID	Cell Weight (kg)	Capacity at 20°C	Capacity at -20°C (RT Charge)	Watt-Hour at -20°C	Energy at -20°C (Wh/kg)	Percent of RT Capacity (%)	Calculated Impedance at -20°C (mOhms) (100% SOC)	Calculated Impedance at -20°C (mOhms) (75% SOC)	Calculated Impedance at -20°C (mOhms) (50% SOC)
SKC01	0.9786	3.3944	3.4556	2.8892	9.738	123.85	81.13	185.01	212.27
SKC03	0.9790	3.3721	3.1607	2.9287	9.933	125.69	81.83	179.15	205.79
SKC04	0.9787	3.3781	3.1347	2.8851	9.716	123.48	81.40	188.59	215.40
SKC05	0.9790	3.3834	3.1473	2.9151	9.842	124.67	81.16	184.07	210.45
SKC06	0.9787	3.3871	3.1596	2.8970	9.780	124.32	81.51	184.14	211.19
SKC07	0.9796	3.3951	3.1727	2.9301	9.903	124.16	81.28	173.38	201.25
SKC08	0.9791	3.3873	3.1256	2.9215	9.9081	125.34	81.25	176.18	202.99
Average	0.9789	3.3857	3.1509	2.9095	9.8314	124.54	81.34	181.63	208.48

The corresponding values at -20°C are ~ 125 Wh/kg (about 85% of the room temperature value) and 210 mOhms (about 9 times that of room temperature value), respectively. Following the formation cycling, the cells have been further characterized for their rate capability from C/10 to 1.5C at different temperatures, i.e., 25, 0, -10, -20 and -30°C. Figs 4 and 5 show the rate capability of these cells at 25°C and 10°C, -10°C and -20°C, respectively.

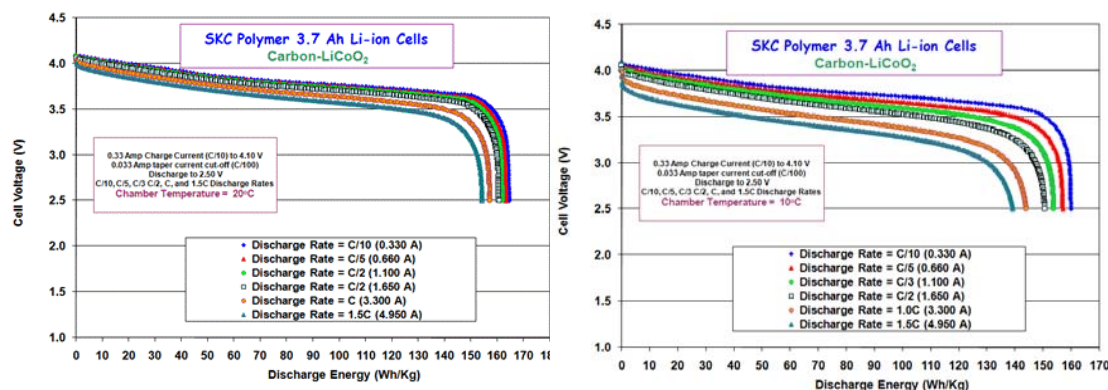


Fig. 4: Rate capability of SKC polymer cells at 25°C and 10°C

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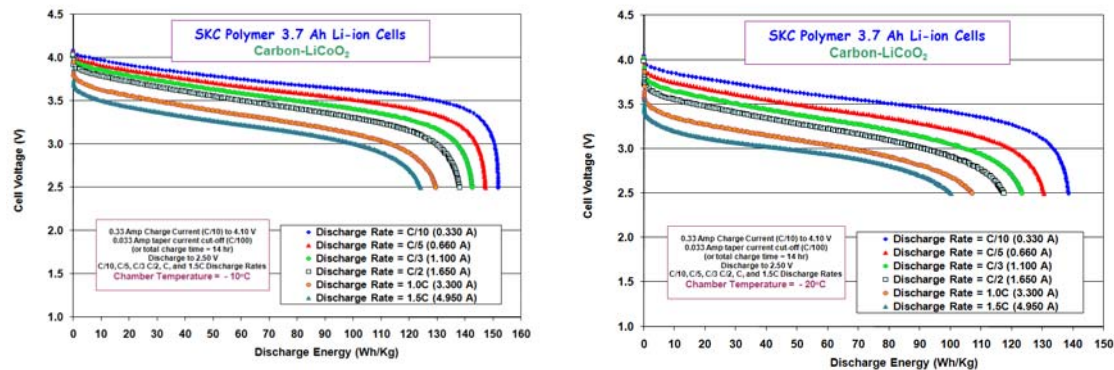


Fig. 5: Rate capability of SKC polymer cells at -10°C and -20°C

As may be seen from the above figure, the cells have good rate capability combined with a good low temperature performance, down to -20°C

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Quallion Pouch Cells

As mentioned above, ten Quallion pouch cells of ~ 4 Ah were available for this study with three different electrolytes, with one being the baseline electrolyte and other two being low temperature electrolytes. These cells with three different electrolytes would enable us to understand the extent of internal pressure build up that would breach the integrity of the cell. Tables 5, 6 and 7 show the discharge capacities and impedance of these cells at 25°C, 0°C and -20°C, respectively.

Table 5: Values of Discharge capacity, energy and impedance of Quallion Pouch cells with different electrolytes at C/5 at 25°C

Cell ID	Cell Weight (Grams)	Cell Weight (kg)	Initial Voltage	Initial Capacity (Ah)	Initial Discharge Rate (A)	Initial Voltage (V)	Calculated Impedance (mOhms) (100% SOC)	Calculated Impedance (mOhms) (80% SOC)	Calculated Impedance (mOhms) (60% SOC)	Electrolyte Type
QA05	78.18	0.0782	3.426	4.3847	16.009	292.19	29.98	39.52	30.44	ED-1
QA06	78.39	0.0784	3.446	4.3864	16.019	294.34	29.83	39.22	29.68	ED-1
QA07	79.11	0.0791	3.451	4.3744	15.951	291.63	30.98	40.74	33.88	ED-1
QA08	79.92	0.0799	3.703	4.3750	15.963	199.73	32.88	42.50	34.10	ED-1
QB04	78.47	0.0785	3.477	4.2974	15.626	199.14	35.86	45.93	37.16	ED-2
QB05	78.69	0.0787	3.461	3.5360	12.640	160.63	65.23	77.21	68.67	ED-2
QB06	79.28	0.0793	3.480	4.2537	15.477	195.22	35.48	47.46	37.92	ED-2
QB07	79.07	0.0791	3.483	4.2530	15.492	195.93	31.43	42.65	32.20	ED-2
QX010	80.31	0.0803	3.431	4.3436	15.018	196.96	33.80	44.10	34.49	Baseline Electrolyte
QX018	79.66	0.0797	3.418	4.3172	15.712	197.24	34.56	45.93	35.78	Baseline Electrolyte
Average	79.21	0.08	3.48	4.25	15.47	195.30	36.91	46.53	37.43	

Table 6: Values of Discharge capacity, energy and impedance of Quallion pouch cells with different electrolytes at C/5 at 0°C

Cell ID	Cell Weight (Grams)	Cell Weight (kg)	Initial Voltage	Capacity at 25°C (Ah)	Capacity at 0°C (Ah)	Capacity at -20°C (Ah)	Watt-Hour at 0°C	Energy at 0°C (Wh/kg)	Percent of RT Capacity (%)	Calculated Impedance (mOhms) (100% SOC)	Calculated Impedance (mOhms) (80% SOC)	Calculated Impedance (mOhms) (60% SOC)	Electrolyte Type
QA05	78.18	0.0782	3.426	4.3847	3.9969	3.8946	14.012	176.96	88.82	75.68	90.10	78.89	ED-1
QA06	78.39	0.0784	3.446	4.3864	3.9893	3.8884	13.972	178.24	88.65	76.75	90.26	79.58	ED-1
QA07	79.11	0.0791	3.451	4.3714	3.9826	3.8836	13.960	176.47	88.84	77.13	90.94	79.65	ED-1
QA08	79.92	0.0799	3.703	4.3750	3.9818	3.8801	13.956	174.62	88.89	77.52	90.71	79.12	ED-1
QB04	78.47	0.0785	3.477	4.2974	3.9034	3.7817	13.565	172.10	88.00	87.89	98.95	96.79	ED-2
QB05	78.69	0.0787	3.461	3.5360	3.6555	3.6749	10.660	135.47	86.96	165.03	175.86	175.62	ED-2
QB06	79.28	0.0793	3.480	4.2537	3.8947	3.7825	13.540	170.88	88.92	84.15	96.74	87.36	ED-2
QB07	79.07	0.0791	3.483	4.2530	3.8850	3.7790	13.559	171.48	88.85	78.89	91.40	82.32	ED-2
QX010	80.31	0.0803	3.431	4.3436	3.848	3.8417	13.716	175.32	88.45	81.64	94.00	83.24	Baseline Electrolyte
QX018	79.66	0.0797	3.418	4.3172	3.9192	3.8179	13.646	171.30	88.41	81.39	96.13	87.36	Baseline Electrolyte
Average	79.21	0.08	3.48	4.25	3.88	3.76	13.40	169.88	88.46	88.81	101.61	92.33	0.00

Table 7: Values of Discharge capacity, energy and impedance of Quallion pouch cells at C/5 at -20°C

Cell ID	Cell Weight (Grams)	Cell Weight (kg)	Initial Voltage	Capacity at 25°C (Ah)	Capacity at -20°C (Ah)	Capacity at -20°C (Ah)	Watt-Hour at -20°C	Energy at -20°C (Wh/kg)	Percent of RT Capacity (%)	Calculated Impedance (mOhms) (100% SOC)	Calculated Impedance (mOhms) (80% SOC)	Calculated Impedance (mOhms) (60% SOC)	Electrolyte Type
QA05	78.18	0.0782	3.426	4.3847	3.3425	2.7709	9.290	117.32	63.19	165.64	295.03	327.15	ED-1
QA06	78.39	0.0784	3.446	4.3864	3.3241	2.8221	9.496	121.13	64.34	162.85	282.75	310.29	ED-1
QA07	79.11	0.0791	3.451	4.3714	3.3074	2.8571	9.649	121.88	65.36	153.58	257.19	282.44	ED-1
QA08	79.92	0.0799	3.703	4.3750	3.3557	2.8742	9.743	121.90	65.69	153.66	243.99	269.63	ED-1
QB04	78.47	0.0785	3.477	4.2974	3.2093	2.6948	9.083	115.75	62.71	188.68	262.00	292.21	ED-2
QB05	78.69	0.0787	3.461	3.5360	2.2174	1.7721	5.708	73.56	56.12	239.34	472.50		ED-2
QB06	79.28	0.0793	3.480	4.2537	3.2304	2.7874	9.189	115.91	63.65	178.87	236.56	257.95	ED-2
QB07	79.07	0.0791	3.483	4.2530	3.2322	2.8113	9.593	121.33	66.10	170.06	213.24	239.34	ED-2
QX010	80.31	0.0803	3.431	4.3436	3.2009	2.6907	9.089	113.10	62.15	150.02	265.63	312.35	Baseline Electrolyte
QX018	79.66	0.0797	3.418	4.3172	3.1846	2.6716	8.966	112.56	61.88	157.17	277.26	334.71	Baseline Electrolyte
Average	79.2080	0.0792	3.478	4.2518	3.1644	2.6881	8.909	113.40	62.5193	171.99	260.42	262.61	

Once again, the specific energies are impressive in the range of 200 Wh/kg, while the impedances are about 30 mOhms, comparable to the SKC polymer cells. As mentioned in the previous section, the higher specific energies may have been achieved with lower anode to cathode capacity ratios. These cells have been assessed for their performance at various low temperatures at different discharge rates. Fig. 6, 7, 8 and 9 illustrate the relative abilities of these cells to operate at low temperatures of -20, -30, -40 and -50°C, respectively.

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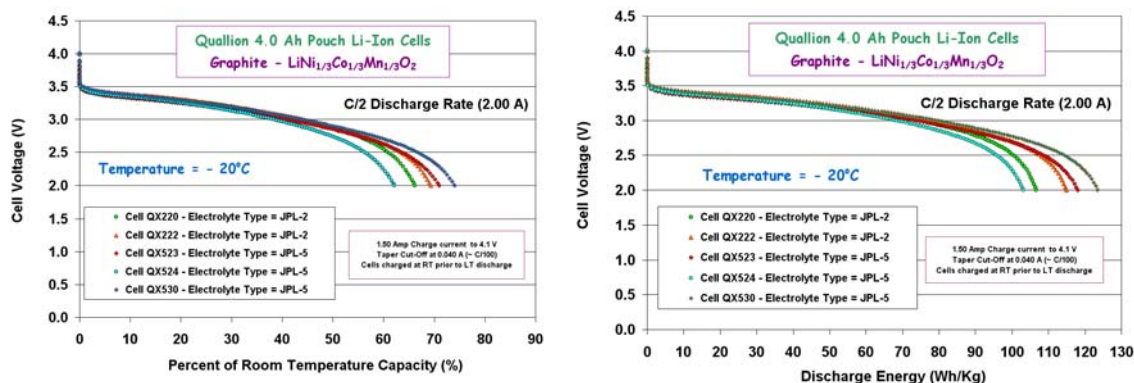


Fig. 6: performance of Quallion pouch cells with different electrolytes at C/2 and -20°C

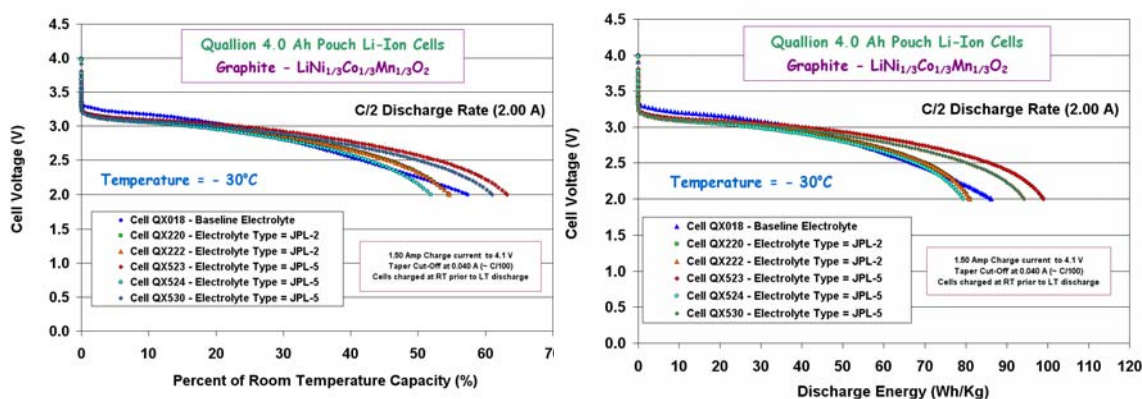


Fig. 7: performance of Quallion pouch cells with different electrolytes at C/2 and -30°C

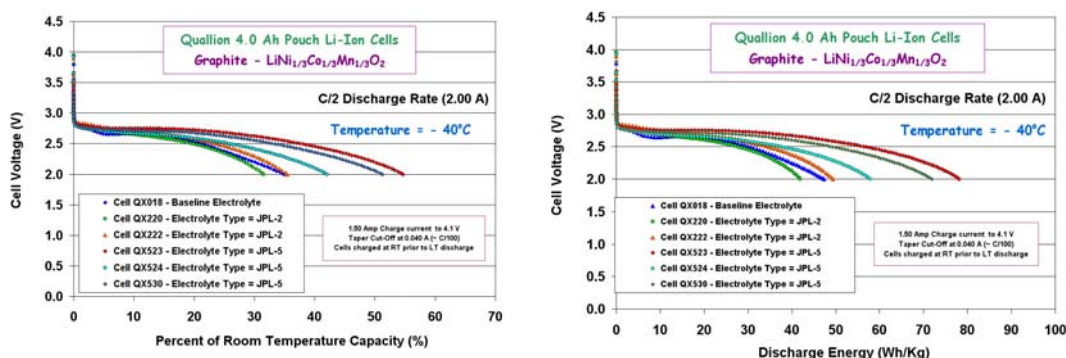



Fig. 8: performance of Quallion pouch cells with different electrolytes at C/2 and -40°C

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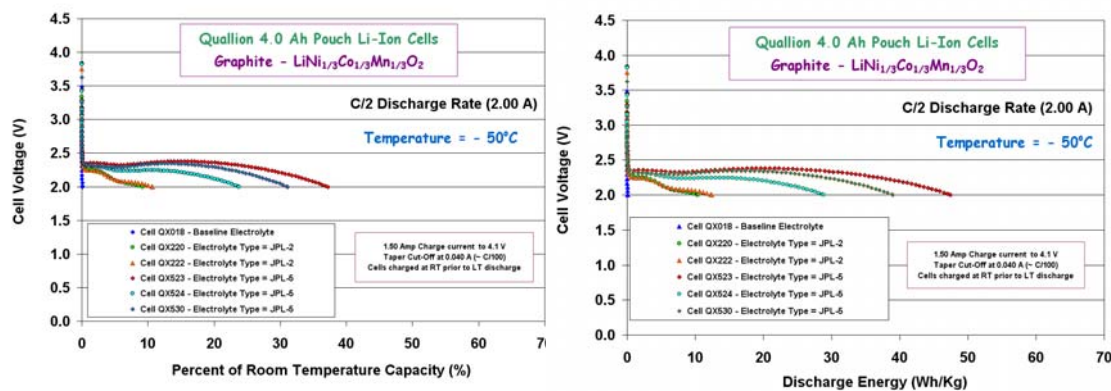


Fig. 9: Performance of Quallion pouch cells with different electrolytes at C/2 and -50°C

As may be seen from the above figures, the two JPL electrolytes tested here provide good low temperature performance, even at a high discharge rate of C/2. The realized capacities to a cut off voltage of 2.0 V are on around 70%, 60%, 40% and 25% of the room temperature values at -20°C, -30°C, -40°C and -50°C, respectively. The baseline electrolyte performed as well as the JPL electrolytes down to -40°C. However, at -50°C, the baseline electrolyte fared poorly compared to JPL electrolytes.

Figure 10 provides a summary of performance with these electrolytes at different low temperatures

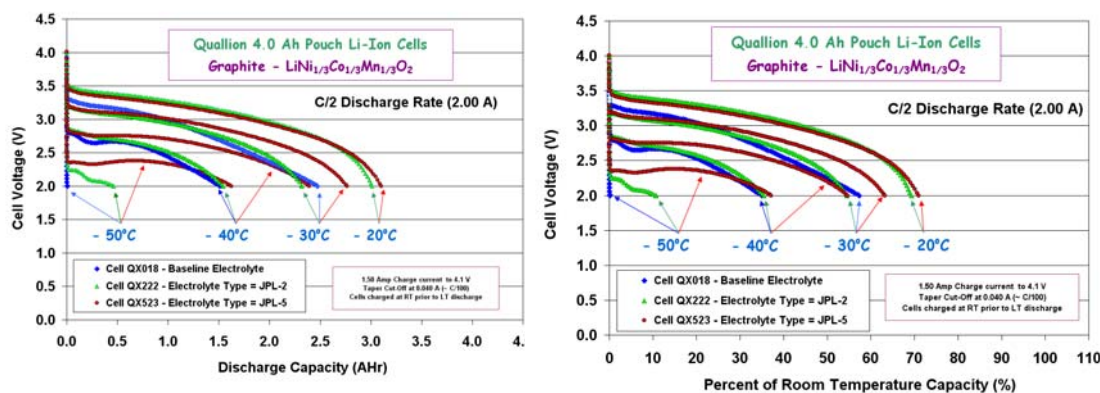



Fig. 10: Comparison of Low temperature performance of Quallion pouch cells with different liquid electrolytes.

It is evident from the figure that the performance of the Quallion baseline electrolyte (composition unknown) is fairly good, almost similar to JPL -3 (all-carbonate) formulation, but

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at -50°C, the baseline electrolyte is non-operational. The JPL-5 electrolyte, which is an ester blend, performed the best at low temperatures, with comparable performance at room temperature.

LTC Pouch Li-ion cells

The pouch Li-ion cells being used for these studies are at least three years old and contain MCMB anode and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode with a conventional liquid electrolytes. These are pseudo-prismatic cells of 1.35 Ah encased in plastic pouches and were procured under the ESMD-ECP program on advanced Li-ion batteries, developed by a team comprising JPL, T/J Technologies and LTC technologies.

Table 8: Performance characteristics at 25°C after formation cycles

Cell Number	Cell ID	Cell Weight (Grams)	Cell Weight (kg)	Initial Voltage	Initial Capacity	Initial Watt-Hours	Initial Wh/kg	Calculated Impedance (mOhms) (100% SOC)	Calculated Impedance (mOhms) (75% SOC)	Watt Hour Efficiency (5th cycle)
SKNASA-1	LTC 1	37.29	0.0373	3.528	1.3839	5.089	136.48	81.4	74.8	97.47
SKMedis-52	LTC 2	33.14	0.0331	3.585	1.4084	5.208	157.14	112.0	90.4	97.54
SKNASA-G	LTC 3	37.66	0.0377	3.521	1.3917	5.122	135.99	70.8	61.4	97.81
SKNASA-J	LTC 4	37.52	0.0375	3.526	1.3838	5.096	135.82	59.8	52.7	98.12
SKNASA-E	LTC 5	37.92	0.0379	3.526	1.3456	4.902	129.28	138.9	132.1	95.02
SKNASA-F	LTC 6	37.43	0.0374	3.530	1.3749	5.059	135.17	70.8	65.1	97.71
SKNASA-B	LTC 7	36.71	0.0367	3.534	1.3765	5.057	137.74	97.7	91.6	97.29
SKNASA-D	LTC 8	37.34	0.0373	3.529	1.3917	5.116	137.01	79.1	74.4	97.63
SKNASA-C	LTC 9	37.59	0.0376	3.516	1.3791	5.085	135.28	58.7	51.5	98.07
SKNASA-A	LTC 10	37.62	0.0376	3.528	1.3884	5.116	136.00	67.4	60.6	97.94
Average		37.02	0.0370	3.532	1.382	5.085	137.59	83.6	75.5	97.5

As shown in the above table, the cells have an average specific energy of ~ 140 Wh/kg and a DC impedance of 75 mOhms. Interestingly, the cells exhibited high cell-to-cell variation mostly in impedance.

During 100% DOD cycling, the cells showed good cycling characteristics over 100 cycles, as shown in Fig. 11.

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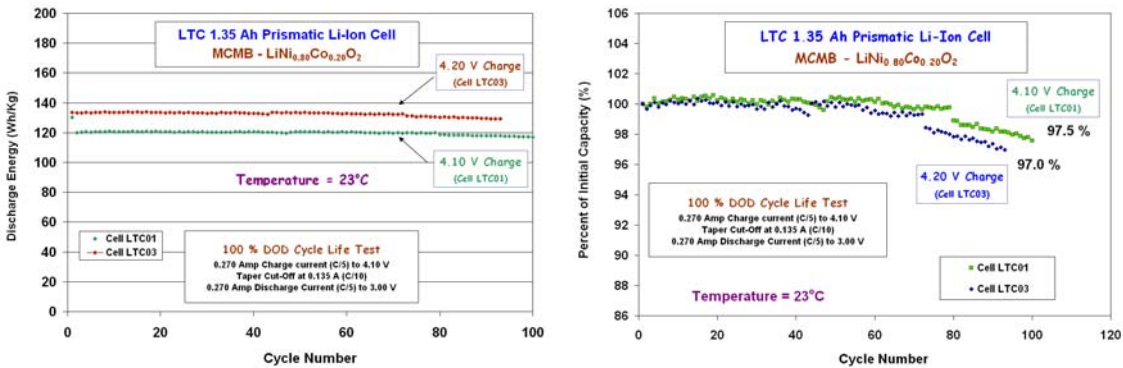


Fig. 11: Cycling of LTC cells at 100% DOD at 25°C.

The cells lose about 2.5% capacity over 100 cycles, when charged to 4.0 V, but this increases to ~ 3% when the charge voltage limit has been increased to 4.2 V. During cycling at low temperature, -20°C, the cells displayed decent cycle life (Fig. 12). The cells exhibit a specific energy of 100 Wh/kg, when charged to 4.2 V, which decreases to ~ 80 Wh/kg when charged to 4.1 V.

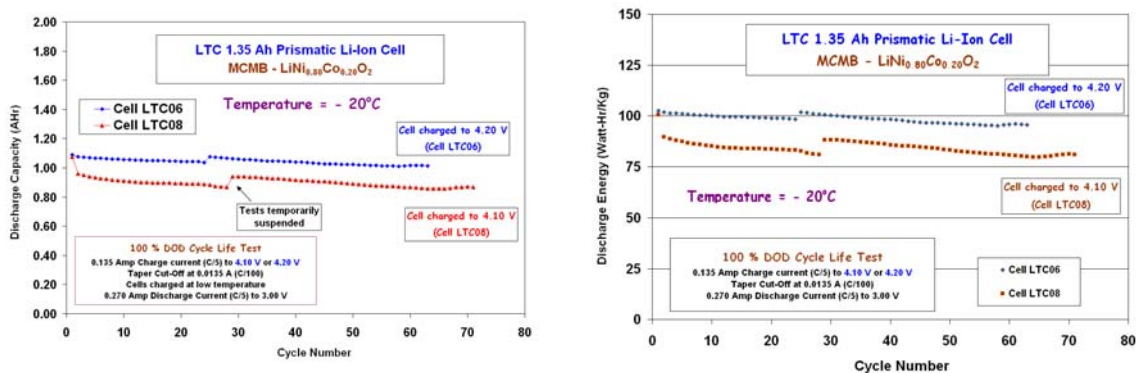


Fig. 12: Cycling of LTC cells at 100% DOD at -20°C.

During LEO cycling at 30% Depth of Discharge, also, the cells exhibited good cycle life (Fig. 13) when charged to 3.95 V or 4.1 V. Over 600 cycles, the cells lost some capacity (almost 10%).

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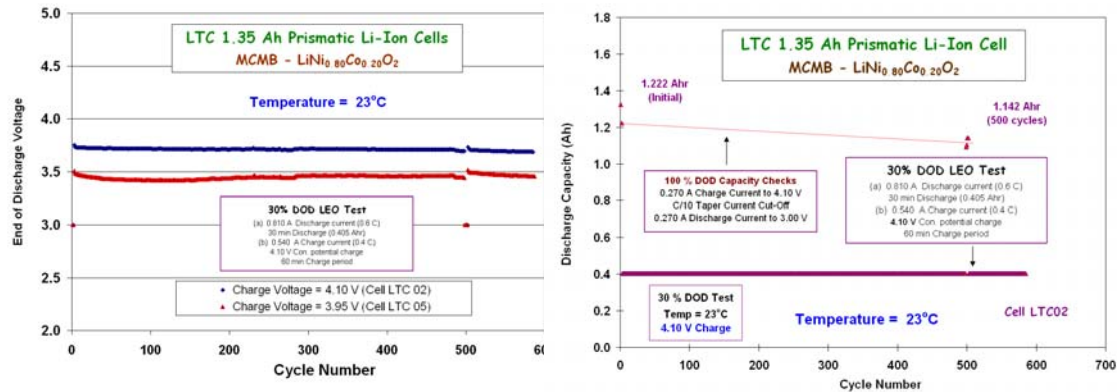


Fig. 13: LEO Cycling of LTC cells at 30% DOD at 25°C, with charge voltages of 3.95 and 4.1 V

Compact Power Li-ion gel polymer Pouch cells

As mentioned above, these cells contain spinel manganese oxide, LiMn_2O_4 as cathode and a gel polymer electrolyte, with a conventional liquid electrolyte as plasticizer. These have a capacity of ~ 7 Ah and are at least four years old. In fact, they have been well tested during this period, as shown in Fig. 14.

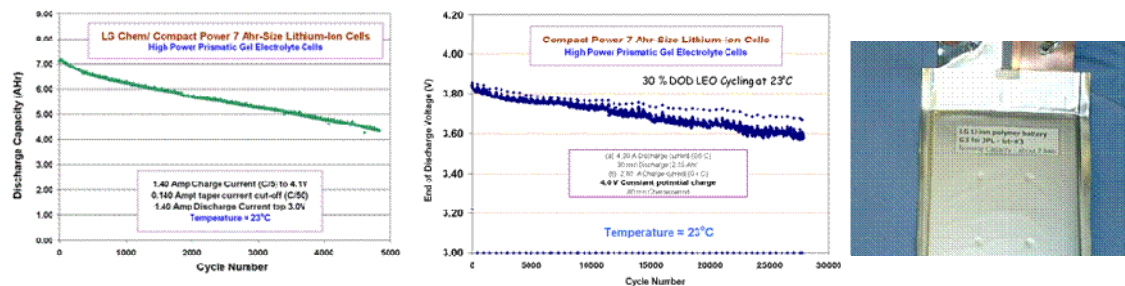


Fig. 14: Cycle life of Compact Power Li-ion cells with gel polymer electrolyte.

The cells display impressive cycling characteristics, both under deep discharge (100% DOD) cycling (almost 5000 cycles to $> 50\%$ capacity) as partial-DOD cycling as in LEO regime (about 29000 cycles at 30% DOD). The long cycle life of these cells implies that the pressure developed within the cell, even when charged to 4.1 V is low enough to be contained within the pouch, or ii) the pouch sealing is adequately strong. Furthermore, these pouch cells showed impressive low

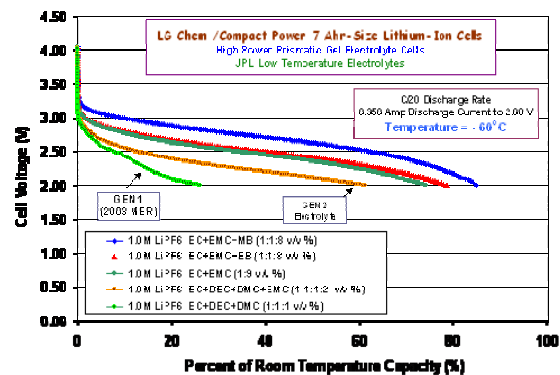



Fig. 15: Low temperature performance of Compact power pouch cells with different JPL electrolytes.

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temperature performance even at -60°C , when the liquid electrolyte (plasticizer) was replaced with various JPL electrolytes (Fig. 15). In any case, this is encouraging and pointing to a likely tolerance to hard vacuum environment as well.

High Temperature Cycling

In order accelerate the failure of the polymer cells upon cycling, the cells were cycled at 60°C , using the same charge voltage (4.1 v, with a taper). Figure 16 shows the performance of Quallion cells with baseline and low temperature electrolyte, LTC cell and SKC cell.

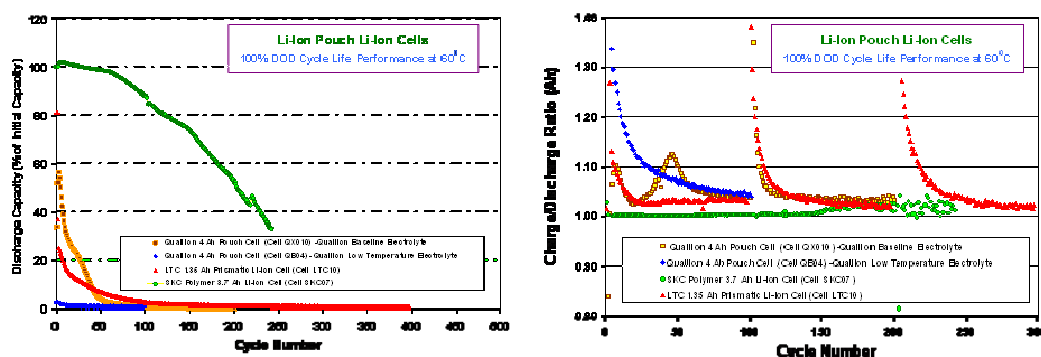


Fig. 16: :High temperature (60°C) cycling of various pouch cells showing rapid capacity fade, accompanied by high charge to discharge capacity ratios.

Interestingly, both Quallion cells failed early, with the low temperature electrolyte failing right away, while the baseline electrolyte cell surviving barely 20-30 cycles. The LTC cell lost the entire capacity within 50 cells. The SKC cell, on the hand, showed good resilience, showing about 50% capacity after 200 cycles. This amount of fade may be expected even in a conventional metal-contained Li-ion cell. The cell hasn't exhibited any rupture which is very encouraging. Among these cells, the cells that failed have unusually high charge to discharge capacity ratios, which suggests that there was considerable amount of electrolyte oxidation, probably internal pressure build up as well. Further results are being analyzed. The differences observed here among these four cells may be attributed to the following factors:


- Nature of electrolyte, especially solvent, which undergoes oxidative degradation during high temperature cycling.
- Amount of electrolyte (normalized to the volume of the cell), which could be higher for the Quallion cells, based on higher energy densities.
- Type of cathode material: Quallion cells, we believe, continued NMC (0.33:0.33:0.33 Ni, Mn and Co) cathodes, while SKC cells contain lithiated cobalt oxide
- Type of electrolyte (either gel or liquid) and finally the
- Pouch seal design

It is difficult to attribute the observed trend to any single factor and further studies are required to gain an understanding on the relative impact of these parameters.

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Thermal Vacuum Cycling

Thermal vacuum cycling studies have been initiated on the representative cells from these sets. The thermal cycling is being performed under non-operating conditions. Following the completion of thermal cycling, the cells will be subjected to a detailed characterization testing, the results of which will be compared with the baseline to assess the resilience of these cells under hard vacuum and thermal cycling.

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Findings, Observations, and Recommendations

Pouch cell configuration provides several advantages over conventional Li-ion cells, i.e., with metallic containers, in terms of specific energy, energy density and packing efficiency. Some of the prototype cells of different types have shown impressive specific energies of 160-200 Wh/kg, at least 20% improvement over their counterparts. One limitation pertaining to a widespread use of pouch cells in aerospace applications is the lack adequate robustness in the hermeticity and integrity of the cells, especially upon electrical and thermal cycling and possibly under hard vacuum environments. This characteristic is a function of electrolyte, type of cathode material (which dictates the charge voltage and hence the extent of electrolyte oxidation) and the pouch seal design. Furthermore, this failure is accelerated at high temperatures, for example, cycling at 60°C, showed clear demarcations among various cells tested. Interestingly, SKC gel polymer showed the greatest resilience to the high temperature cycling and may be expected to exhibit similar tolerance to vacuum also. It is recommended that the selected prototype cells be tested in the anticipated thermal and vacuum environments before hand, before putting them for use. As a diagnostic, the cells may be subjected to an accelerated cycling test at a high temperature, after establishing a correlation between such acceleration and the expected cycle life at room temperature. Such a correlation may be established by performing accelerated cycling tests at various temperatures, e.g., 25°C, 40, 45, 50 and 55°C, and analyzing the data to get the Arrhenius factors and activation energies for the capacity fade and life-limiting processes.

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Appendix G. Li-Ion Cell PTC Device Withstanding Thresholds

E. Darcy, F. Davies, J. Jeevarajan, G. Varela and P. Patel
NASA-Johnson Space Center, Houston, TX, USA
and
B. Strangways and T. Nelson
Symmetry Resources, Inc., Arab, AL, USA

Abstract


Through iterative testing, we assessed the performance characteristics and safety limitations of the resettable, positive thermal coefficient (PTC) current limiting device of 4 commercial 18650 cell designs. Specifically, we determined the withstanding voltage/power thresholds at which the cell would emit odor, visibly leak, become irreversibly damaged, and/or fail catastrophically. Significant differences in voltage level thresholds exist between the 4 cell designs. For example, at 45.2V (11S) of total series voltage, the heat generated during the PTC device trip transition and during less than 2 minutes of holding the trip state of the Sony HC cell design causes its insulating crimp seal to melt and cause a cell internal short. In contrast at 61.6V (15S), the PTC device of the Panasonic cell design suffered only benign irreversible electrical damage without emitting odors or signs of leakage. The PTC device performance of each cell design was significantly different. However, when tripped, all 4 PTC device designs acted uniformly as a thermal regulator generating between 3.2W and 3.5W of resistive heat while in the trip state. This is independent of the in-rush current/power that caused its transition into the trip state. This heat must be properly dissipated in densely-packed, large battery designs to allow the cell and its PTC device to safely perform. High voltage external short conditions can contribute to electrical overstress of the PTC device leading to catastrophic failures, but so can densely-packed, low voltage conditions.

Objectives

The objectives were to characterize the performance of the current limiting positive thermal coefficient (PTC) device in commercial 18650 Li-ion cell designs and determine the external short voltage withstanding thresholds at which it will emit odor, visibility leak, sustain irreversible electrical damage, and/or fail catastrophically. The ultimate purpose of this effort is establish test methods for establishing external short abuse tolerance of cell designs to ensure safe large capacity and/or high voltage battery designs.

Introduction

The battery design concept utilizing small commercial cells to achieve large capacity batteries has proven to be very successful, safe, and cost-effective. This is in a large part because of the very tight performance uniformity, safety, and low-cost of the commercial cells selected.


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Unfortunately, the safety features of commercial 18650 Li-ion cells have been proven ineffective when assembled into certain high voltage and/or high capacity battery module assemblies. Specifically, the cell's over-current, resettable, polymeric switch (aka, PTC device) can ignite when subjected to high voltage short conditions.

From 2001 to 2004, NASA pursued a Space Shuttle upgrade requiring a very high voltage (360V) and large energy (28 kWh) lithium ion battery design to power its Auxiliary Power Unit. Several subscale test battery modules from 35V to 100V were assembled and intentionally exposed to external shorts to demonstrate the catastrophic hazard. Adding a diode in parallel with every 6 cells in series showed promise in tests with 180V battery assemblies. However, more work is required to fully prove its effectiveness.

In 2004, a low voltage (2S), large capacity (66P) battery module suffered a catastrophic thermal runaway when inadvertently exposed to an external short while inside a commercial cargo carrying Boeing 747, within 30 minutes of take-off. The cells were at 50% state-of-charge at the time of the incident. Nevertheless, the highly nested and densely packed battery module design most likely prevented the cell PTCs from preventing catastrophic fire.

The cell PTC device is located in the top header of the crimped-seal header assembly of the 18650 cell design. It is held in place and isolated from the negative polarity of the can by the crimp seal as shown in Fig. 1. The PTC device consists of two metal coated sides sandwiching a matrix of a crystalline polyethylene polymer composite containing dispersed conductive particles, usually carbon black. The resistance of the PTC device increases with temperature (Positive Temperature Coefficient, PTC). The device has a resistance that increases sharply with temperature as shown in Fig. 2. When a short is applied to a cell, the elevated currents cause the device to self-heat and move to a high resistance state in which most of the cell voltage is across the device, but the current is significantly reduced. As long as the short is maintained, the PTC device produces enough heat to keep itself in this state (lower current being offset by greater voltage drop across device) as shown in Fig. 3.

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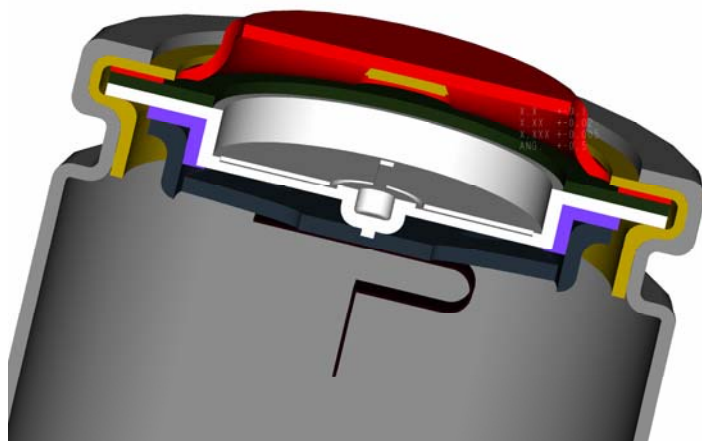


Figure 1. CAD representation of the top header assembly of the Sony 18650 HC cell. The PTC device is the green annulus disc sandwich between the red top cover and the white current interrupt device (CID).

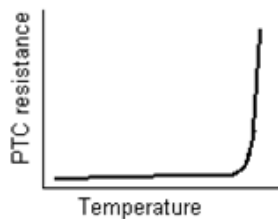


Figure 2. Typical PTC device resistance's dependence on temperature.

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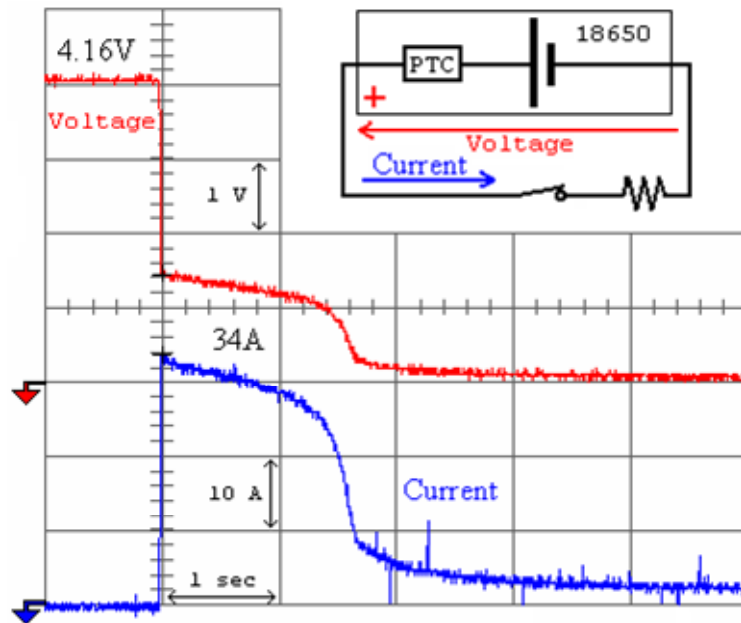


Figure 3. Typical current and voltage transient profiles of cell with a PTC device exposed to a short circuit. In-rush maximum current is 34A. Trip transition takes over 2 seconds to achieve a steady state hold current or nearly 1A.

Method


Four currently available commercial 18650 lithium ion cell designs were evaluated;

- Sony US18650S (also known as 18650HC) rated at 1.5Ah
- E-one Moli Energy, ICR-18650J rated at 2.4Ah
- Sanyo Energy, UR18650F rated at 2.2Ah
- Panasonic, CGR-18650C rated at 2.15 Ah

These cells under test were provided to Symmetry Resources, Inc., where the testing was conducted [1]. In addition, over 30 units of a commercial 18650 high rate cell design (without a PTC) were provided.

First, the following protocol was followed to accept the cells from each design;

- perform serialization,
- visual,
- mass (± 5 mg),
- dimensions,
- OCV (± 1 mV),
- CCV (± 1 mV) to calculate DC internal resistance,
- 1 kHz AC impedance (± 10 mohms),
- and measure PTC hold current resistance to ± 2 mohms at room temperature on 5 randomly chosen cells from each cell design.

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The external short tests were conducted with n high power 18650 cells in series, charged to 4.1V/cell, to drive the required voltage through the cell under test, resulting in $n+1$ cells in series. Using high power cells without PTCs provides a relevant power source for the cell under test and obviates issues with sluggish power supplies. The cell under test was charged to 4.2V to a limiting taper current of 50 mA. The resistance of short circuit loop of the test was adjusted for each test condition to achieve an approximate 16A in-rush current with each cell design as shown in Fig. 4. Throughout each test, cell voltage, current, and two cell skin temperatures (near top and bottom of cell) were recorded at 1 Hz minimum. During the PTC trip transition, cell voltage and current was recorded at 1 MHz sampling rate. Each test was allowed to continue with cell in tripped state until 60 minutes after maximum temperature had been achieved.

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Fig. 4. Electrical schematic of test set-up

The cell under test was visually inspected during the trip test and the strength of any odors coming from the cells was noted. Then the cell was allowed to rest overnight before performing another visual inspection, mass measurement, measuring its AC impedance at 1 kHz measured along with its remaining discharge capacity with its DC resistance.

After all the cell tests were completed with all 4 cell designs, the cells that were tested at the thresholds were disassembled to remove the cell header assembly for further analysis and impedance tests. In addition, unused samples from each cell design were disassembled to obtain mass breakdowns of all separable components and cell axial and radial potted cross cuts were achieved to allow dimensional measurements of key features of each cell design.

Results

The pre-test acceptance results are summarized in Table 1. Note that the Panasonic design has lower internal resistance, AC impedance, and lower virgin PTC resistance. Of the four designs, it's achieves the highest specific energy. The Moli, Panasonic, and Sanyo designs all achieved more than 180 Wh/kg at C/2 to 3.2V at room temperature. The Sony cell achieves 130 Wh/kg when discharged at C/10 to 2.5V at room temperature.


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Table 1. Pre-test Acceptance Measurements

Cell Design	OCV (V)	CCV (V)	DC Re (mΩ)	AC Imp (mΩ)	PTC Virgin Re (mΩ)	Mass (g)
Sony US18650S	3.838	3.590	124.0	64.7	22.4	40.641
Moli ICR-18650J	3.806	3.580	113.2	60.7	21.9	47.284
Sanyo UR18650F	3.788	3.585	101.8	55.0	19.1	45.359
Panasonic CGR-18650C	3.778	3.582	98.0	46.6	13.4	43.261

Table 2. Cell Mass Breakdown

Component	Moli Mass (g)	Panasonic Mass (g)	Sanyo Mass (g)	Sony HC (g)
Cell	47.109	43.319	45.343	40.467
Positive Insulator	0.044	0.0350	0.036	0.034
PVC Sleeve	0.456	0.325	0.603	0.305
Bare cell	46.609	42.960	44.709	40.128
Electrolyte (by extraction wt. loss) (4 cells, respectively)	1.58, 1.14, 1.5, 0.71	1.988, 2.110, 1.364	1.740, 1.836, 0.949	1.859
Seal & Positive cover ass'y (Seal, button, PTC, CID, collector, insulator, & contact plate (only Pan))	1.313	1.221	1.225	1.293
Seal	0.162	0.093	0.158	0.173
Button	0.759	0.476	0.479	0.639
PTC	0.093	0.099	0.111	0.104
CID	0.189	0.069	0.075	0.218
Collector	0.110	0.052	0.054	0.120
		0.072		0.037
		0.349	0.334	
Positive insulator (internal)	0.053	0.145	0.052	0.068
Negative insulator (internal)	0.054	0.132	0.059	0.082
Jelly roll	36.553	35.273	36.141	28.006
Positive [Al] Electrode (*)	18.567	18.498	17.834	16.058
Negative [Cu] Electrode (*)	12.029	12.451	10.372	9.352
Separator, 2 piece	1.562	1.649	1.933	1.547
Roll Pin insert	1.991	0.788	0.626	NA


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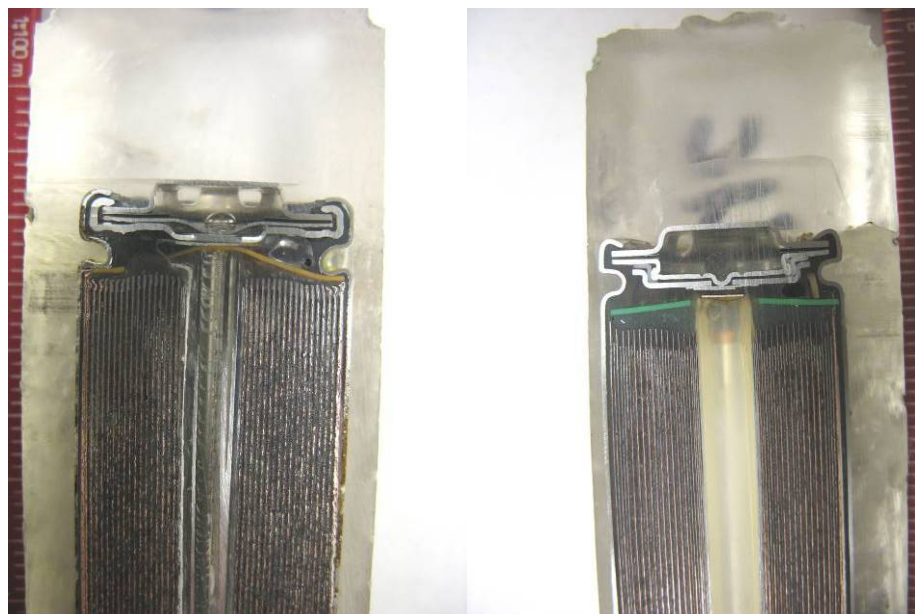
*Note that electrode material flaked off during Destructive Physical Analysis (DPA), separator mass contains portions of electrode materials and electrode mass does not reconcile to jelly roll mass

The mass breakdown of all the separable components in each cell design is presented in Table 2. Note that the roll pin insert of the Moli cell is almost 2g and nearly 5% of cell mass and that the Sony cell does not have one.

Photographs of the Sony, Moli, Sanyo, and Panasonic cell DPA are presented in Appendix A. The cross cuts of the top header assemblies reveal very significant design differences. The Sanyo and the Panasonic designs have their PTC device and CID insulated with a crimp connection separately insulated from the can crimp seal. As Figures 5A thru 5D show, the



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Figures 5A-D. Axial cross cuts of the head assembly showing the double insulator crimp designs of the Panasonic (left top) and the Sanyo (left bottom) and the single insulator crimp designs of the Moli (top right) and Sony (bottom right).


In the majority of the cells under test, the resistance of the test circuit, including the cells was adjusted to yield an in-rush current of ~16A. As the PTC started its trip transition, the time to trip was measured, the power dissipated in the tripped PTC was calculated, and, at equilibrium, the top and bottom skin temperatures of the cell were recorded. All these values are listed in Table 3.

Table 3. Cell PTC performance parameters with 16A in-rush current

Cell Design	Time to trip	Calc PTC W	Top Temp	Bottom Temp
	sec	mΩ	degC	degC
Sony US18650S	4.6	3.21	75.3	61.0
Moli ICR-18650J	12.0	3.38	73.5	62.5
Sanyo UR18650F	11.5	3.27	71.9	60.5
Panasonic CGR-18650C	27.2	3.34	74.0	61.8

It's very interesting how uniformly the PTC device regulates the power dissipated in the tripped state within all these cell designs despite their differences in virgin resistances and time to trip. This explains the uniformity in the cell temperatures at thermal equilibrium.

The complete PTC withstanding voltage test data sets are the Appendix B. The number of high power cells in series was set by iteration in order to determine the maximum number of cells in series would ensure no or very slight odors and no irreversible PTC device damage. Damage was

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defined as post trip resistance that was > 3 times that of its virgin (never tripped) resistance. Note the manufacturer datasheets on the PTC device specifies that post trip resistance of undamaged devices are always < 2 times that of virgin resistance of the same device. A summary is presented as follows with n representing the number time the test was repeated with similar results to support the stated findings;

- Moli results
 - 7S is maximum series count to prevent PTC damage and leakage ($n=3$)
 - 4S is maximum series count to prevent slight odor from seal ($n=3$)
- Sanyo results
 - 3S is maximum series count to prevent PTC damage ($n=3$)
 - 8S is maximum series count to prevent odor from seal ($n=3$)
- Sony results
 - 3S is maximum series count to prevent PTC electrical damage ($n=3$)
 - 10S is maximum series count to prevent smoking the PTC ($n=1$)
 - at 11S, seal damage led to an internal short ($n=1$)
 - at 12S, rapid, severe electrical damage to PTC without seal damage ($n=1$)
 - Its PTC has the slowest tripping transition
- Panasonic results
 - 7S yields no odor, no leakage, but slight electrical damage ($n=3$)
 - 11S and 15S yields no odor, no leakage, but some electrical damage ($n=1$)

Note that electrolyte in the Moli cells is very pungent and much more readily detected by human smell than the other cell electrolytes. The Sanyo and Sony cells must be tripped at low voltages $< 4S$ to not suffer electrical damage to the PTC device, while the Moli and Panasonic are more tolerant ($>7S$). The Panasonic is the lone standout for which were not able to make it leak or emit any odors, even after high voltage (55.9V) was applied across the cell and its PTC device during the 15S test. A close up of the Panasonic header (Fig 6.) clearly shows how the CID collector plate has a thick perimeter edge that is crimped with an insulator to insulate the CID collector from the CID vent disc and seat it with the PTC device and top button. This subassembly is crimped together inside the main crimp seal with the cell can. On Fig. 7, the separable components of the Panasonic header assembly are shown. The crimp plate with the thick perimeter edge that is crimped exists in the Sanyo cell design, but not in the Moli and Sony designs.


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Figure 6. Close-up of cross-cut of Panasonic Header Assembly.

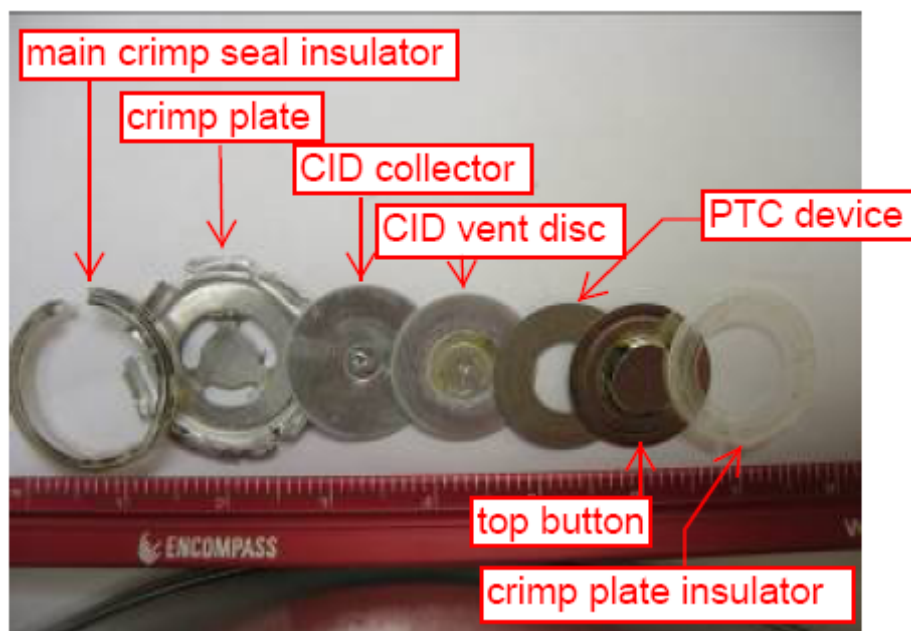


Figure 7. Panasonic Header Assembly components after DPA.

With 11 cells in series (including the cell under test), the Sony cell PTC device showed nominal trip performance and held for 1.37 minutes before failing nearly catastrophically. The resultant heat dissipated in the header assembly caused the crimp seal isolation to fail, resulting in a cell internal short.

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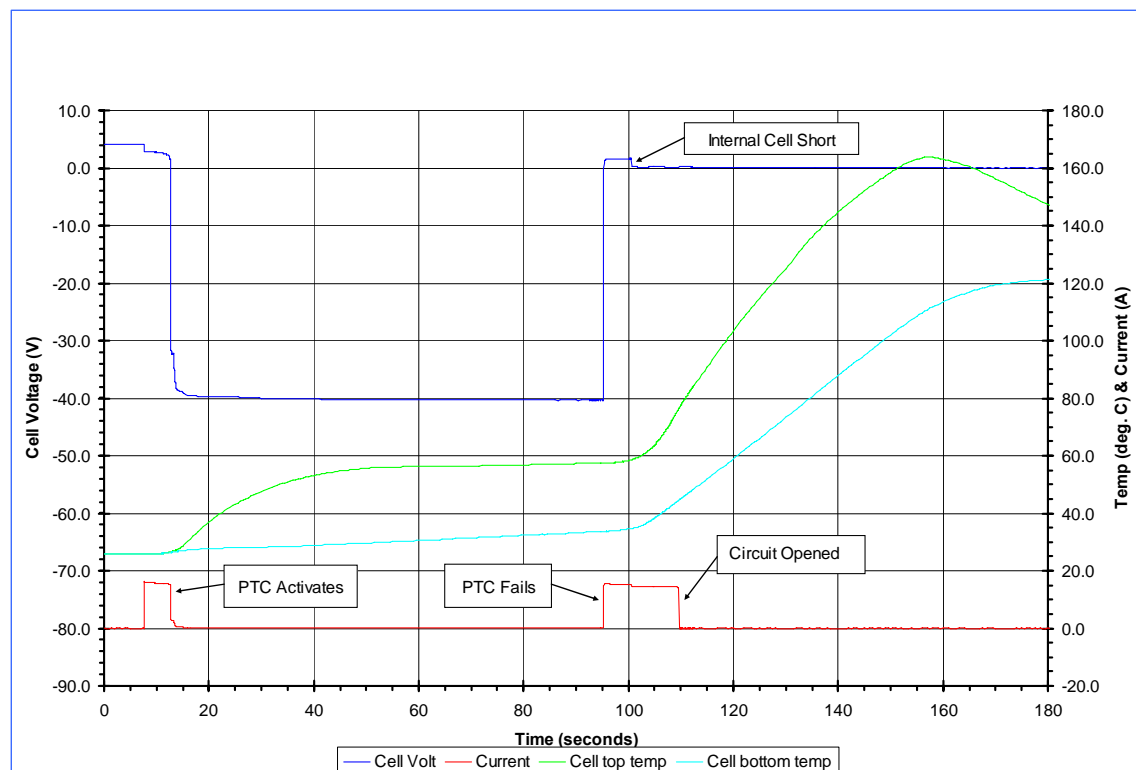


Figure 7. Li-Ion Cell PTC Withstanding Voltage Test. Sony US18650S (Hard Carbon); Cell #71P020; Initial 3 minutes of test. Charged @0.7A to 4.2VV, 4.2V to 0.05A 10S COTS 18650HR string in series, 2.29 ohm circuit resistance.

As shown in Fig. 7, the PTC device trips nominally with 16A of in-rush current, but the approximate -40V across it during and after trip transition cause more heat than the crimp seal could tolerate. Cell voltage jumped to near zero and the external circuit resumed pumping 16A through the cell when the PTC device failed in a closed circuit conditions. Then within 12 seconds, the external short circuit was manually opened prior to evacuating the area for safety reasons, and cell skin temperatures rose to a peak of 163.9 °C on the top and 121.9 °C at the bottom within 60 seconds. Thereafter, the cell ran out of juice and temperatures subsided. The cell lost 102 mg of mass as a result of the seal failure shown in Figs 8 & 9 after DPA.



Sony 11S video.wmv

The above object is the video recording of the Sony cell test with 11S. After the PTC device trips and holds for over a minute, a small thin stream of smoke emerges followed by a larger puff when the PTC device fails closed circuit.

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Figures 8 & 9. Sony cell and cell header assembly after 11S short circuit test which internally shorted. Note the thermally damage crimp seal (black/blue) and positive tab insulator (green).

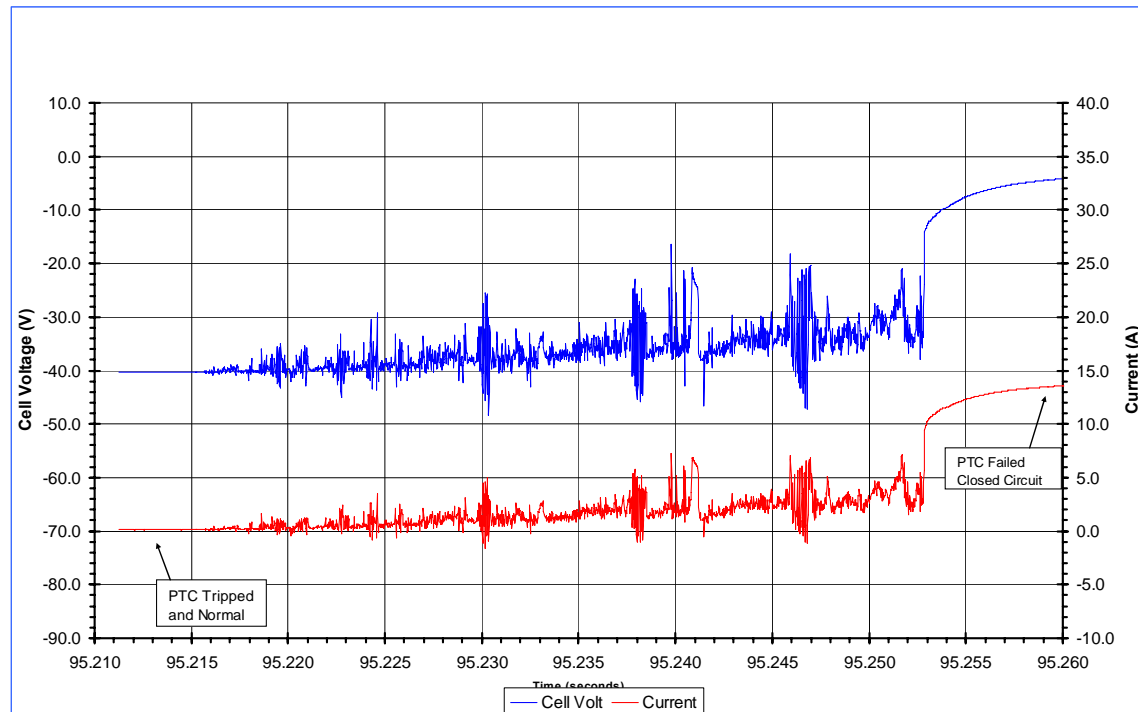
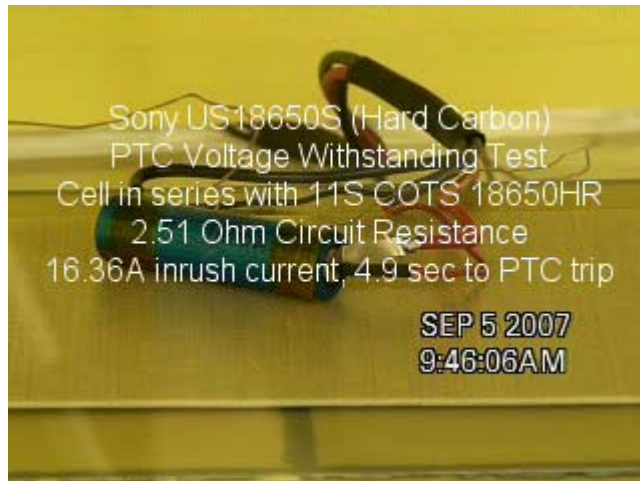


Figure 10. The voltage and current transitions from a nominally tripped Sony PTC device to a closed circuit condition during its failure with 12 cells in series (12S).

At 12S, the transition of failure of the PTC to hold its trip state and failed closed circuit occurred with 40 ms as shown in Fig. 10. One quick dark puff of smoke from the cell header was detected in the video recording of the event in the object below.

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Sony 12S video.wmv

Note: Snapshots from the video.

It's interesting that at 12S, the additional power dissipated through the PTC device is sufficient to instantly smoke it into a low resistance (shorted) condition, but without sufficient energy dissipation to cause the crimp seal to fail catastrophically as happened in the 11S test.

Overall, the Panasonic cell design demonstrated superior seal under the abusive short circuit conditions performed herein. Even under 15S conditions, the cell did not emit odor or leak electrolyte. It's possible that the double crimped design plays a significant role.

Conclusions

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- The cell PTC device has voltage/power limitations that vary with cell design, which when exceeded can lead to catastrophic cell failures.
- When held in the tripped state the cell PTC device generates 3.2 to 3.5W of heat regardless of the in-rush current and voltage applied to trip it.
- The thresholds for odor emittance and slight leakage must be determined with in-situ visual observation of the cell under test.
- Our test method developed herein was successful at determining the design limitations of a cell PTC device.

Recommendations

- Due to the hazardous consequences of an overwhelmed cell PTC device, it's therefore very important to characterize its performance and determine its voltage/power withstanding thresholds.
- The power (3.2 to 3.5W) of heat generated in a tripped cell PTC device must be properly dissipated to prevent its hazardous failure in a multi-cell battery configuration. The thermal dissipation paths for this heat must be analyzed within the battery design and validated to ensure preservation of the cell PTC device's safety feature.
- Careful selection of bypass diode design is needed to mitigate that limitation as per the guidelines provided by Davies [2].

References

- [1] Tim Nelson, "Cell PTC Withstanding Voltage Thresholds", Report #71P, tbd
[2] Frank Davies, "Design Guidelines for Diode Protection Scheme for Cell PTC Devices", tbd

Attachments:

DPA Photos of the Cell Designs

Sony US18650S (HC) and US18650VT (HR) Designs

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Cell PTC Withstanding Voltage Test


NASA-JSC Contract- NNJ07HG03P
Sony HC 18650J, Li-ion

PHYSICAL ATTRIBUTES:

Component	Mass (g)	Dimensions (in)	Dimensions (mm)
Cell	40.467		
Positive Insulator	0.034		
PVC Sleeve	0.305		
Bare cell	40.128		
Electrolyte (by extraction wt. loss)	1.859		
Seal & Positive cover assembly	1.293		
Seal	0.173		
Button	0.639	0.633"D x 0.016"th	16.1 D x 0.4 th
PTC	0.104	0.633"OD x 0.360"ID x 0.012"th	16.1 OD x 9.1 ID x 0.3 th
CID	0.218	0.632"D x 0.013"th	16.1 D x 0.3 th
Collector	0.120	0.515"D x 0.015"th	13.1 D x 0.4 th
Collector insulator	0.037		
Positive roll insulator (internal)	0.068	0.661"D x 0.017"th	16.8 D x 0.4 th
Negative roll insulator (internal)	0.082	0.674"D x 0.017"th	17.1 D x 0.4 th
Jelly roll	28.006	2.29"L x 0.67"D	58.2 L x 17.0 D
Positive [Al] Electrode	16.058	20.47"L x 2.09"W x 0.0075"th	520 L x 53 W x 0.19 th
Negative [Cu] Electrode	9.352	21.30"L x 2.20"W x 0.007"th	541 L x 56 W x 0.18 th
Al & Cu electrode foils		< 0.001"th	< 0.025 th
Separator, 2 piece	1.547	25.71"L x 2.28"W x 0.001"th	653 L x 58 W x 0.025 th
Outside Wrap Tape	0.103		
Roll Pin insert	NA		

SRI- Job #71P
01/16/07

Symmetry Resources, Inc.

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Cell PTC Withstanding Voltage Test

NASA-JSC Contract-
Sony HC

NNJ07HG03P
18650, Li-ion

NNJ07HE43P	Sony HC Li-Ion 18650-DPA		
			
Cell	Bare Cell	Positive	Bare Positive
			
Pos end open	Button Assembly w/can	Button Assembly	Button Assembly
			
CID & Collector	CID & Collector	Cover components	Jelly roll (pos)
			
Roll securing tape	Positive electrode	Negative electrode	Negative electrode

SRI- Job #71P
01/16/07

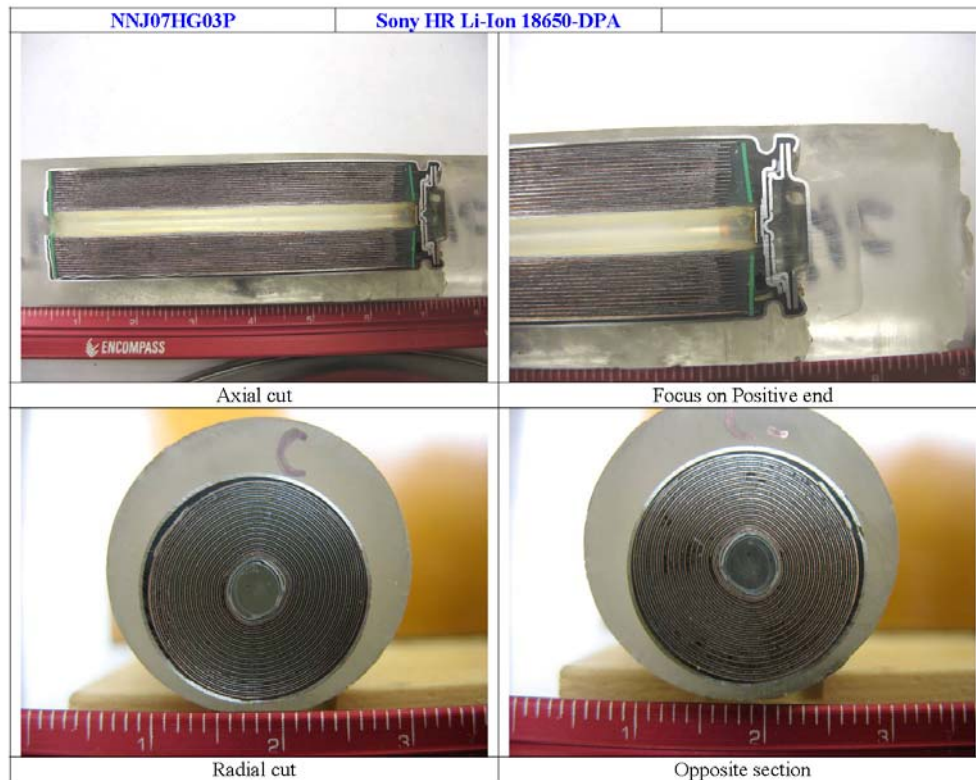
Symmetry Resources, Inc.

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Cell PTC Withstanding Voltage Test

NASA-JSC Contract-
Sony HC

NNJ07HG03P
18650, Li-ion



SRI- Job #71P
01/16/07

Symmetry Resources, Inc.

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Cell PTC Withstanding Voltage Test


NASA-JSC Contract- NNJ07HG03P
Sony HR 18650, Li-ion

PHYSICAL ATTRIBUTES:

Component	Mass (g)	Dimensions (in)	Dimensions (mm)
Cell	41.045		
Positive Insulator	0.036		
PVC Sleeve	0.279		
Bare cell	40.730		
Electrolyte (by extraction wt. loss)	0.813		
Seal & Positive cover assembly	1.551		
Seal	0.169		
Button	1.014	0.637"D x 0.028"th	16.2 D x 0.7 th
PTC	NA		
CID	0.215	0.631"D x 0.015"th	16.0 D x 0.4 th
Collector	0.116		
Collector insulator	0.037		
Positive roll insulator (internal)	0.068	0.661"D x 0.017"th	16.8 D x 0.4 th
Negative roll insulator (internal)	0.083	0.674"D x 0.017"th	17.1 D x 0.4 th
Jelly roll	29.162	2.32"L x 0.68"D	58.9 L x 17.3 D
Positive [Al] Electrode (*)	12.111	27.76"L x 2.17"W x 0.005"th	705 L x 55 W x 0.13 th
Negative [Cu] Electrode (*)	13.445	28.70"L x 2.28"W x 0.005"th	729 L x 58 W x 0.13 th
Al & Cu electrode foils		0.001"th	0.025 th
Separator, 2 piece (*)	2.032	2.32"W x 0.001"th. Material adhered to electrodes during DPA, which rendered a condition to prevent length measurement.	
Outside Wrap Tape	1.204	9.45"L x 2.17"W x 0.004"th	240 L x 55 W x 0.10 th
Roll Pin insert	NA		
* Electrode material flaked off during DPA, which does not allow for complete reconciliation of weights. Primarily on the negative electrode.			

SRI- Job #71P
01/16/07

Symmetry Resources, Inc.

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Cell PTC Withstanding Voltage Test

NASA-JSC Contract-
Sony HR

NNJ07HG03P
18650, Li-ion

NNJ07HE43P	Sony HR Li-Ion 18650-DPA		
			
Cell	Bare Cell	Positive	Bare Positive
			
Pos end open	Button Assembly	Button Assembly	CID & Collector
			
CID & Collector	Cover components	Jelly roll (pos)	Jelly roll (neg)
			
Roll w/tape	Positive electrode	Negative electrode	Negative electrode

SRI- Job #71P
01/16/07

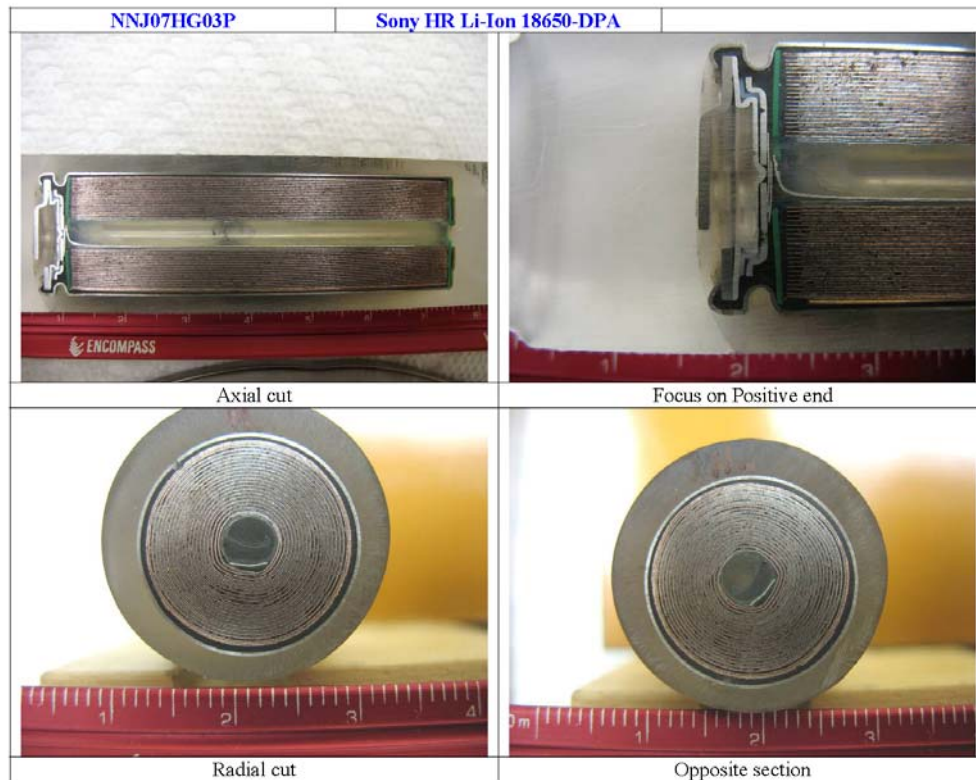
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Cell PTC Withstanding Voltage Test


NASA-JSC Contract-
Sony HR

NNJ07HG03P
18650, Li-ion



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Moli ICR-18650J Design

18650 Redesign for the EMU LIB

NASA-JSC Contract- NNJ07HG03P
SRI Job # 71A
December 5, 2007

Testing
Performed by
Symmetry Resources, Inc.
Arab, Alabama

Written by
Tim J. Nelson

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Destructive Physical Analysis and Cross sections


NASA-JSC Contract- NNJ07HG03P
E-One Moli Cell Model #- ICR 18650J, Li-ion
Lot Date Code- Lot 0111 (April 2007)

PHYSICAL ATTRIBUTES:

Component	Mass (g)	Dimensions (in)	Dimensions (mm)
Cell	47.109		
Positive Insulator	0.044		
PVC Sleeve	0.456		
Bare cell	46.609		
Electrolyte (by extraction wt. loss) (4 cells, respectively)	1.58, 1.14, 1.5, 0.71		
Seal & Positive cover assembly	1.313		
Seal	0.162		
Button	0.759	0.63"D x 0.02"thickness (th)	16.0D x 05th
PTC	0.093	0.63"OD x 0.39"ID x 0.0125"th	16.0OD x 9.9ID x 0.32th
CID	0.189	0.63"D x 0.013"th	16.0D x 0.33th
Collector	0.110	0.472"D x 0.02"th	12.0D x 0.5th
Positive insulator (internal)	0.053	0.66"D x 0.01"th	16.8 D x 0.25th
Negative insulator (internal)	0.054	0.66"D x 0.01"th	16.8D x 0.25th
Jelly roll	36.553	2.4"L x 0.68"D	61.0L x 17.3D
Positive [Al] Electrode (*)	18.567	24.8"L x 2.2"W x 0.006"th	629.9L x 55.9W x 0.15th
Negative [Cu] Electrode (*)	12.029	25.7"L x 2.3"W x 0.007"th	652.8L x 58.4W x 0.18th
Separator, 2 piece(*)	1.562	29.5"L & 28.9"L x 2.36"W x 0.001"th	749.3L & 734.1L x 59.9W x 0.025th
Roll Pin insert	1.991	2.318"L x 0.126"D	58.9L x 3.2D
*Electrode material flaked off during DPA, separator mass contains portions of electrode materials and electrode mass does not reconcile to jelly roll mass			

SRI- Job #71A
12/05/07

Symmetry Resources, Inc.

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Destructive Physical Analysis and Cross sections


NASA-JSC Contract-
E-One Moli Cell Model #-
Lot Date Code-

NNJ07HG03P
ICR 18650J, Li-ion
Lot 0111 (April 2007)

NNJ07HG03P	Moli Li-Ion ICR 18650J-DPA	Lot 0111 (Apr, 2007)	
			
Cell	Bare Cell	Positive	Bare Positive
			
Pos end open	Button Assembly w/can	Button Assembly	Bottom Insulator
			
CID & Collector	Cover components	Jelly roll	Roll securing tape
			
Positive electrode with roll pin	Roll pin	Positive electrode	Negative electrode

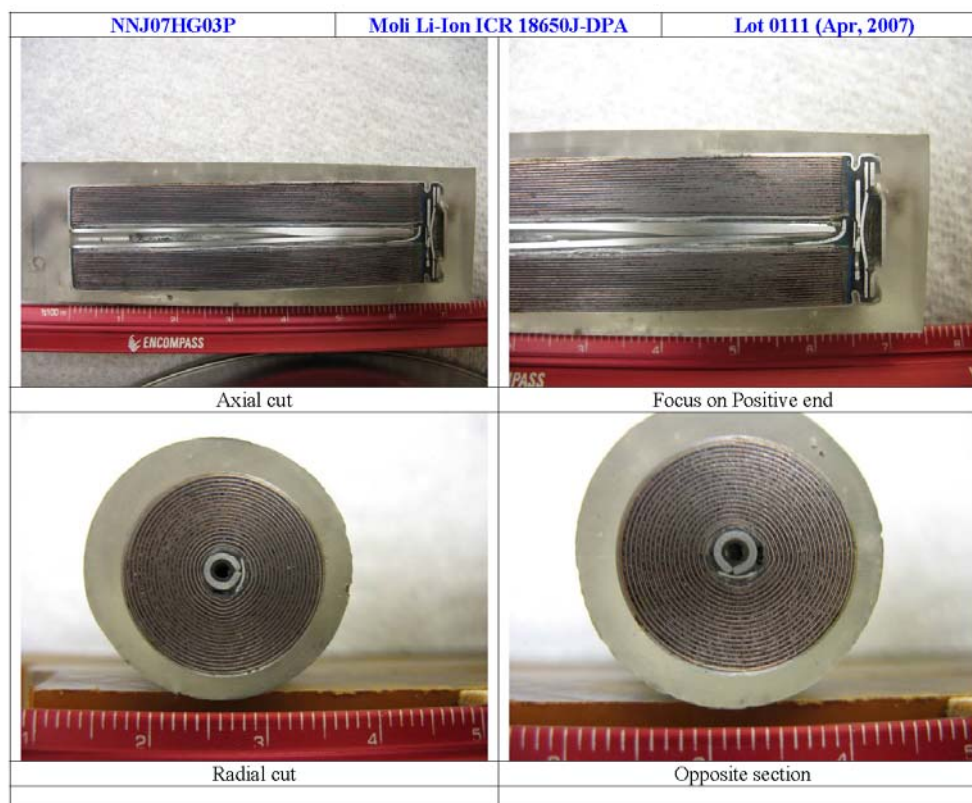
SRI- Job #71A
12/05/07

Symmetry Resources, Inc.

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Destructive Physical Analysis and Cross sections

NASA-JSC Contract- NNJ07HG03P
E-One Moli Cell Model #- ICR 18650J, Li-ion
Lot Date Code- Lot 0111 (April 2007)



SRI- Job #71A
12/05/07

Symmetry Resources, Inc.

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Sanyo UR18650F Design

Cell PTC Withstanding Voltage Tests

NASA-JSC Contract-
Sanyo


NNJ07HG03P
UR18650F, Li-ion

PHYSICAL ATTRIBUTES:

Component	Mass (g)	Dimensions (in)	Dimensions (mm)
Cell	45.343		
Positive Insulator	0.036		
PVC Sleeve	0.603		
Bare cell	44.709		
Electrolyte (by extraction wt. loss) (3 cells, respectively)	1.740, 1.836, 0.949		
Positive cover assembly w/seal, (Collector, CID, PTC, Button-w/insulator-seal)	1.225		
Seal	0.158		
Button	0.479	0.590"D x 0.013"th	15.0 D x 0.3 th
PTC	0.111	0.589"OD X 0.125"ID X 0.014"th	15.0 OD x 3.2 ID x 0.4 th
CID	0.075	0.585"D x 0.006"th	14.9 D x 0.2 th
CID-PTC-Button insulator	0.054		
Collector w/some material removed during DPA	0.334		
Positive roll insulator (internal)	0.052	0.67"D x 0.012"th	17.0 D x 0.3 th
Negative roll insulator (internal)	0.059	0.65"D x 0.012"th	16.5 D x 0.3 th
Jelly roll	36.141	2.29"L x 0.68"D	58.2 L x 17.3 D
Positive [Al] Electrode (*)	17.834	28.78"L x 2.20"W x 0.007"th	731 L x 56 W x 0.18 th
Negative [Cu] Electrode (*)	10.372	25.55"L x 2.24"W x 0.007"th	649 L x 57 W x 0.18 th
Pos Elect. (secondary measure) (b)	18.550		
Neg Elect. (secondary measure) (b)	12.054		
Al & Cu electrode foils		0.001"th	0.025 th
Separator, 2 piece (most electrode materials removed, includes a small amount of tape securing roll)	1.933	2.28"W x 0.001"th. Material adhered to electrodes during dpa, which rendered a condition preventing length measurement.	
Separator (secondary measure) (b)	2.002		
Roll Pin insert	0.626	2.329"L x 0.11"D	59.2 L x 2.9 D
* Electrode material primarily flaked off the negative electrode during DPA, which does not allow for complete reconciliation of weights.			
(b) For verification of negative electrode integrity, a second cell was disassembled. Negative electrode material was easily removed from the substrate and adhered to portions of the separator. Again, material lost in DPA which affects primarily the weight of the neg. electrode.			

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Cell PTC Withstanding Voltage Tests

NASA-JSC Contract-
Sanyo


NNJ07HG03P
UR18650F, Li-ion

NNJ07HE43P		Sanyo Li-ion UR18650F-DPA	
			
Cell	Bare Cell	Positive	Bare Positive
			
Pos end open	Button Assembly w/can	Button Assembly tilted	Button-PTC-CID-Collector assembly
			
Seal & Cover assembly	Cover assembly -tab connection	Cover assembly components	Components(opposite)
			
Jelly roll (pos)	Roll securing tape	Positive electrode	Negative electrode

Notes: All references are in mm. The positive button/PTC/CID/collector is a manufactured part, which encases all the components in an aluminum structure. The positive button, PTC and CID are held together with a plastic insulator. A small thin square Al sheet is welded to the Al collector and the CID is welded to the small square thin Al plate. All the components are closed in this collector assembly, in which it is placed in a plastic seal. The component is welded to the positive tab and crimp closed in the cell can (actual manufacture sequence may differ from this verbal description). This button component is similar in construction as compared to the Panasonic cell. A black-brai type sealant substance is liberally used in the sealing areas.

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Cell PTC Withstanding Voltage Tests

NASA-JSC Contract-
Sanyo

NNJ07HG03P
UR18650F, Li-ion



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Panasonic CGR-18650C Design

Cell PTC Withstanding Voltage Test

NASA-JSC Contract- NNJ07HE43P
Panasonic CGR18650C
Sleeve Lot Marking- K (7516)

PHYSICAL ATTRIBUTES:

Component	Mass (g)	Dimensions (in)	Dimensions (mm)
Cell	43.319		
Positive Insulator	0.0350		
PVC Sleeve	0.325		
Bare cell	42.960		
Electrolyte (by extraction wt. loss) (3 cells, respectively)	1.988, 2.110, 1.364		
Positive cover assembly w/seal, (Collector, CID, PTC, Button-w/insulator-seal)	1.221		
Seal	0.093		
Button	0.476	0.592"D x 0.008"th	15.0D x 0.2 th
PTC	0.099	0.592"OD X 0.292"ID X 0.013"th	15.0 OD x 7.4 ID x 0.3 th
CID	0.069	0.585"D x 0.006"th	14.9 D x 0.2 th
CID (contact plate to collector)	0.052	0.611"D x 0.004"th	15.5 D x 0.1 th
Insulator for (CID-PTC-Button)	0.072		
Collector w/some material removed during DPA	0.349		
Positive roll insulator (internal)	0.145	0.672"D x 0.019"th	17.1 D x 0.48 th
Negative roll insulator (internal)	0.132	0.654"D x 0.013"th	16.6 D x 0.33 th
Jelly roll	35.273	2.37"L x 0.70"D	60.2 L x 17.8 D
Positive [Al] Electrode (*)	18.498	27.36"L x 2.20"W x 0.006"th	695 L x 56 W x 0.15 th
Negative [Cu] Electrode (*)	12.451	25.39"L x 2.28"W x 0.007"th	645 L x 58 W x 0.18 th
Al & Cu electrode foils		0.001"th	0.025 th
Separator, 2 piece	1.649	29.8"L x 2.3"W x 0.001"th.	758 L x 59 W x 0.025 th
Roll Pin insert	0.788	2.303"L x 0.099"D	58.5 L x 2.5 D
* Electrode material flaked off electrodes during DPA, which does not allow for complete reconciliation of weights.			

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Destructive Physical Analysis and Cross sections

NASA-JSC Contract-
Panasonic
Sleeve Lot Marking-


NNJ07HE43P
CGR18650C
K (7516)

NNJ07HE43P		Panasonic Li-ion CGR18650c-DPA	
			
Cell	Bare Cell	Positive	Bare Positive
			
Pos end open	Neg end open	Button Assembly	Button (cover) assembly
			
Cover assembly -tab connection	Collector - Collector Contact-CID (w/insulator)	Cover assembly components	Components(opposite)
			
Jelly roll (pos)	Roll w/green securing tape	Positive electrode	Negative electrode

Notes: All references are in mm. Cell very wet with electrolyte, positive & negative roll insulators are stiff and have the appearance of a linen/laminated phenolic sheet versus flexible plastics used in other observed cell manufacturers. The positive button/PTC/CID/collector is a manufactured part, which encases all the components in an aluminum structure. The positive button, PTC and CID are held together with a plastic insulator. The CID is welded to a thin Al plate at one central point, while the thin Al plate is welded to the substantial Al collector. All the components are closed in this collector assembly, in which it is placed in a plastic seal. The component is welded to the positive tab and crimp closed in the cell can. This button component is similar in construction to the Sanyo cell.

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1/04/08

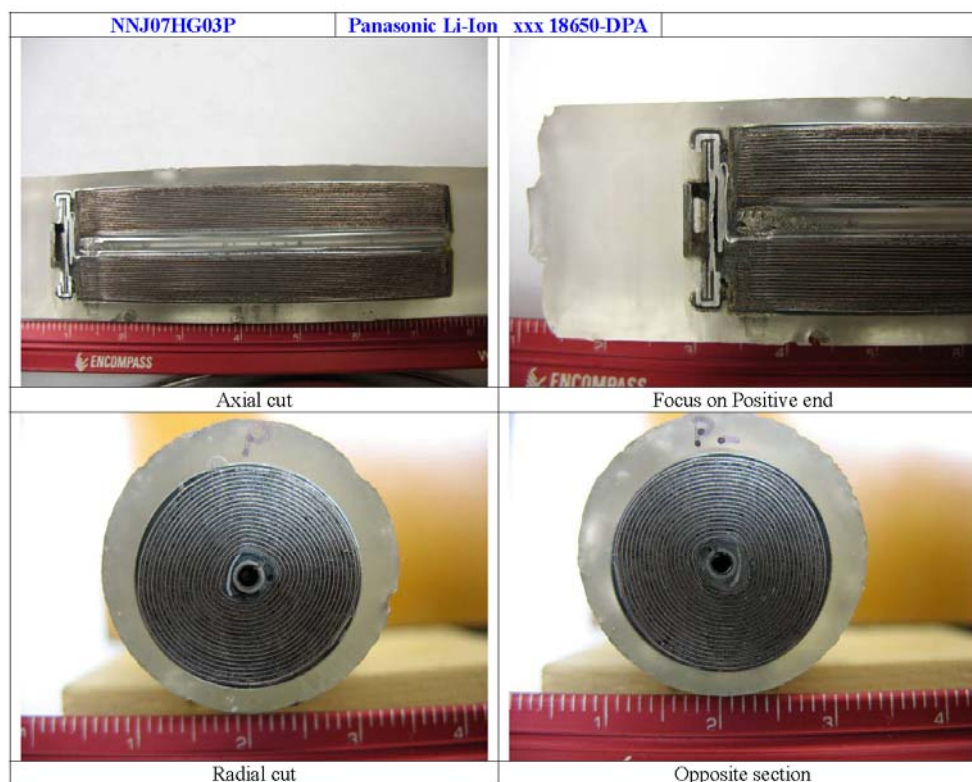
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Destructive Physical Analysis and Cross sections

NASA-JSC Contract-
Panasonic
Sleeve Lot Marking-

NNJ07HE43P
CGR18650C
K (7516)



SRI- Job #71P
1/04/08

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PTC Device Test Data Spreadsheets

PTC Voltage Withstanding
Sony US18650S (Hard Carbon)
Tested with Commercial 18650HR String in Series with Test Cell
External Circuit Resistance Set to Create Approx. 16-17A inrush current
Test Cell Charged at 0.7A to 4.2V, 4.2V to 0.05A

PTC Voltage Withstanding
Sony US18650S (Hard Carbon)
Tested with Commercial 18650HR String in Series with Test Cell
External Circuit Resistance Set to Create Approx. 16-17A inrush current
Test Cell Charged at 0.7A to 4.2V, 4.2V to 0.05A

Cell ID #	HR Strg Series Cell Count	Ext. Circuit Resist (ohms)	Recorder File #	Inrush Current (A)	Trip Time (s)	10sec Avg Trip Pwr Calc PTC Pwr (W)	Post-Trip Stabilized Avgs					Observations, Post-Test Electrolyte detect	Calculated Eff Internal Resistance (mohm) from OCV/CCV								Discharge Cap. (A-h)	AC Impedance (mohm)			Mass (g)		Post-test Header only	
							Cell V	Current (A)	Calc PTC Pwr (W)	Top Temp (C)	Bottom Temp (C)		Pre-Test OCV	Calc. Re	OCV	Post-Test OCV	Calc. Re	Delta	Pre-Test	Post-test		Delta	Pre-Test	Post-Test	Delta	AC Imp. (mohm)	DC	
71P001	9	2.07	0003	16.49	4.5	19.41	-36.16	0.079	3.18	72.8	58.3	no odor	3.836	3.592	122.4	4.093	3.754	169.7	47.2	1.163	66.2	118.5	52.3	40.732	40.730	-0.002		
71P002	11	2.51	0007	16.36	4.9	N/A	N/A	N/A	N/A	N/A	N/A	PTC smoked, no odor, DPA to test seal	3.837	3.592	122.8	4.137	3.908	114.6	-8.2	1.270	66.5	65.9	-0.6	40.796	40.779	-0.007	31.2	
71P003	7	1.64	0013	16.58	4.6	16.28	-28.00	0.100	3.21	74.5	60.9	no odor	3.838	3.593	123.0	4.091	3.788	151.7	28.6	1.146	65.9	104.1	38.2	40.635	40.632	-0.003	53.7	
71P004	8	1.87	0016	16.48	4.8	20.80	-32.06	0.089	3.22	75.5	60.8	no odor	3.840	3.596	122.0	4.089	3.756	166.7	44.6	1.144	63.1	116.1	53.0	40.736	40.729	-0.007	58.1	
71P005	8	1.87	0018	16.56	4.4	20.03	-32.06	0.088	3.18	75.2	60.6	no odor	3.837	3.585	125.9	4.096	3.743	176.7	50.7	1.147	65.8	124.1	58.3	40.667	40.659	-0.008		
71P006	6	1.87	0020	16.55	4.3	19.64	-32.07	0.089	3.22	76.4	61.1	no odor, DPA to assess electrical damage	3.837	3.589	124.1	4.091	3.742	174.7	50.6	1.158	64.3	124.5	60.2	40.690	40.686	-0.004	open	
71P007	9	2.07	0023	16.49	4.9	21.89	-36.14	0.081	3.26	75.2	61.2	no odor	3.837	3.589	124.3	4.076	3.733	171.7	47.4	1.097	64.0	119.0	55.0	40.620	40.613	-0.007		
71P008	9	2.07	0025	16.49	4.4	19.14	-36.15	0.079	3.18	75.0	61.3	no odor	3.838	3.590	124.0	4.101	3.767	167.2	43.1	1.161	64.8	116.5	51.7	40.550	40.545	-0.005		
71P009	7	1.65	0027	16.59	4.4	20.29	-27.97	0.100	3.21	75.1	61.0	no odor	3.838	3.589	124.8	4.085	3.771	157.2	32.4	1.131	65.1	107.2	42.1	40.655	40.650	-0.005	53.1	
71P010	7	1.65	0030	16.57	4.6	19.44	-27.98	0.099	3.18	74.8	61.3	no odor, DPA to assess electrical damage	3.837	3.588	124.8	4.086	3.638	224.2	99.4	1.102	64.7	162.7	98.0	40.626	40.618	-0.008	59.4	
71P011	4	1.01	0036	16.93	3.9	19.31	-15.69	0.163	3.22	76.9	61.2	no odor	3.837	3.587	125.1	4.038	3.726	156.2	31.1	1.024	65.1	107.4	42.3	40.609	40.605	-0.004		
71P012	4	1.01	0038	16.90	4.4	18.49	-15.67	0.165	3.26	74.9	61.1	no odor	3.836	3.592	122.3	4.038	3.719	159.7	37.3	1.023	62.2	110.9	48.7	40.658	40.654	-0.004		
71P013	4	1.01	0040	17.00	4.4	18.99	-15.69	0.161	3.18	77.1	63.0	no odor	3.837	3.590	123.8	4.046	3.731	157.7	33.9	1.039	64.3	108.8	44.5	40.579	40.577	-0.002		
71P014	3	0.81	0046	16.27	5.2	17.90	-11.619	0.202	3.17	74.8	60.4	no odor	3.837	3.590	123.9	4.020	3.723	148.6	24.8	0.979	63.9	99.6	35.7	40.635	40.632	-0.003		
71P015	3	0.81	0049	16.30	4.6	18.13	-11.609	0.205	3.22	74.4	61.3	no odor	3.838	3.587	125.5	4.011	3.697	157.2	31.7	0.944	65.5	108.4	42.9	40.585	40.582	-0.003		
71P016	3	0.81	0050	16.14	4.9	17.78	-11.591	0.206	3.23	77.6	61.6	no odor	3.836	3.587	124.5	4.012	3.695	158.7	34.2	0.951	64.6	109.9	45.3	40.600	40.598	-0.002		
71P017	4	1.03	0052	16.35	4.9	18.54	N/A	N/A	N/A	50.6 max	29.9 max	10sec tripped hold, no odor	3.838	3.591	123.7	4.170	3.847	161.7	37.9	1.297	64.7	112.9	48.2	40.698	40.696	-0.002		
71P018*	0	0.051	0059	33.94	0.63	12.21	0.0457	0.878	3.51	81.1	64.2	no odor	3.840	3.594	123.0	3.900	3.602	149.1	26.1	N/A	63.6	97.0	33.4	40.654	40.652	-0.002		
71P019	4	0.49	0061	32.75	0.52	20.20	-15.80	0.166	3.30	77.6	62.9	sleeve & washer thermal damage, no odor	3.839	3.594	122.6	4.039	3.636	201.7	79.1	0.987	63.0	779.4	716.4	40.676	40.671	-0.005	62.7	
71P020	10	2.29	0064	16.36	5.0	19.75				163.9 max	121.9 max	PTC held for 1.37min, failed, cell shorted	3.838	3.592	123.0	0.000	N/A	N/A	N/A	N/A	64.5	13.3	-51.2	40.681	40.579	-0.102	40.2	
71P021	2	0.28	0069	32.01	0.48	17.54	-7.855	0.265	3.16	76.2	62.0	no odor	3.837	3.587	125.2	3.983	3.657	163.2	38.0	0.867	65.7	114.1	48.4	40.632	40.628	-0.004		
71P022	4	0.49	0082	32.33	0.43	21.10	-15.82	0.160	3.19	75.9	63.3	no odor	3.838	3.590	124.1	4.046	3.724	161.2	37.1	1.035	64.6	112.7	48.1	40.635	40.630	-0.005		
71P023													3.838	3.587	125.3						65.4			40.650				
71P024													3.838	3.586	126.0						66.1			40.594				
71P025													3.837	3.588	124.8						64.4			40.535				
71P026													3.838	3.587	125.6						66.0			40.552				
71P027													3.837	3.589	123.8						63.7			40.680				
71P028													3.837	3.590	123.7						68.2			40.602				
71P029													3.837	3.591	123.0						63.5			40.592				
71P030													3.838	3.595	121.5						62.7			40.705				

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Appendix H. Current Interrupt Device (CID) Arcing in Li-Ion Cells

E. Darcy, F. Davies, J. Jeevarajan, G. Varela and P. Patel
NASA-Johnson Space Center, Houston, TX, USA
and
B. Strangways and T. Nelson
Symmetry Resources, Inc., Arab, AL, USA

Abstract

Through iterative testing, we assessed the performance characteristics and determined the susceptibility to arcing of the current interrupt device (CID) of 3 commercial 18650 cell designs under high voltage conditions. This effort tests if at a certain high voltage threshold, an overcharge condition of a series cell string has the risk that the first cell CID to activate may arc and ignite the flammable electrolyte vapors in the cell.

Objectives


The objective were to characterize the performance of the CID in 3 commercial 18650 Li-ion cell designs and determine the series voltage thresholds at which arcing becomes a safety concern. A secondary purpose of this effort is establish test methods for establishing the overcharge protection limits tolerance of cell designs to help ensure safe high voltage battery designs.

Introduction

Rechargeable 18650 Lithium Ion cells are being pursued as the building blocks for several high voltage, high capacity aerospace batteries. Even though these batteries don't solely rely on the cell's CID for overcharge protection to prevent a catastrophic failure, we want to know under what conditions is the feature a valid control in high voltage batteries. The CID functions by severing an electrical connection within the cell due to an over-pressurization of the cell during an overcharge condition. Cell designs with the CID feature contain an additive that generates gas pressure when driven into overcharge. At a certain pressure, the CID expands and interrupts all external current flow to the cell. This is an irreversible feature that permanently open circuits the cell.

If higher pressures develop internally for other reasons, the cell rupture vent located on the CID plate will relieve cell pressure irreversibly. See Figure 1 for details on a generic header assembly.

The safety concern investigated herein is at what voltage threshold does arcing become a concern during CID activation. Several previous overcharge tests of multi cell battery assemblies have indicated that conditions can exists where the CID will partially open and reseal itself before irreversibly activating. Can this "switch bounce" behavior produce a dangerous arcing condition?

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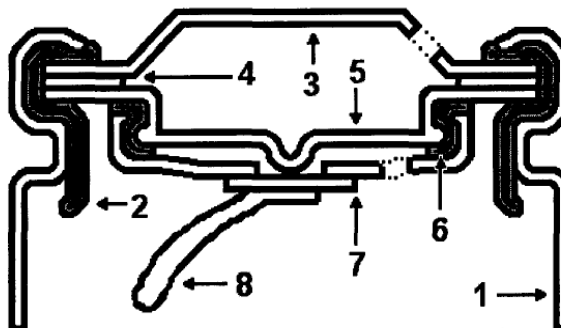


Figure 1: Test Article Cross Section

1.	Cell housing.
2.	Insulating seal.
3.	End cap
4.	PTC
5.	CID (Current Interrupt Device)
6.	CID insulator.
7.	CID back plate.
8.	Electrode tab.

Shape:	Cylinder
Diameter:	18.4 mm (includes sleeve)
Height:	6-10 mm

Method

Three currently available commercial 18650 lithium ion cell designs were evaluated;

- e) Sony US18650S (also known as 18650HC) rated at 1.5Ah
- f) E-one Moli Energy, ICR-18650J rated at 2.4Ah
- g) Sony US18650VT, a 1Ah, high rate cell design without a PTC device

These cells under test were provided to Symmetry Resources, Inc., where the testing was conducted.

The high rate cell capacity performance was evaluated at various rates (from C rate to 18C) at ambient conditions. Charging was at 1A to 4.1V followed with a 50mA taper termination. The cell was allowed to rest 10 minutes before discharging at the various rates with several 10A, 10s pulse to allow an internal resistance calculation. See Figure 2 for the voltage profiles and Figure 3 for the corresponding internal resistance profile.

A destructive physical analysis (DPA) of each cell design was conducted to assess cell construction feature differences and to measure the mass of each separable component of each

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design. Radial and axial cross cut examinations of each cell were obtained to allow dimensional measurements of design features. These were obtained by puncturing a hole in the cell, centrifuging as much of the electrolyte out as possible, back filling with an epoxy, mounting it in that epoxy, axially and radially cutting it, and polishing the cut as necessary.

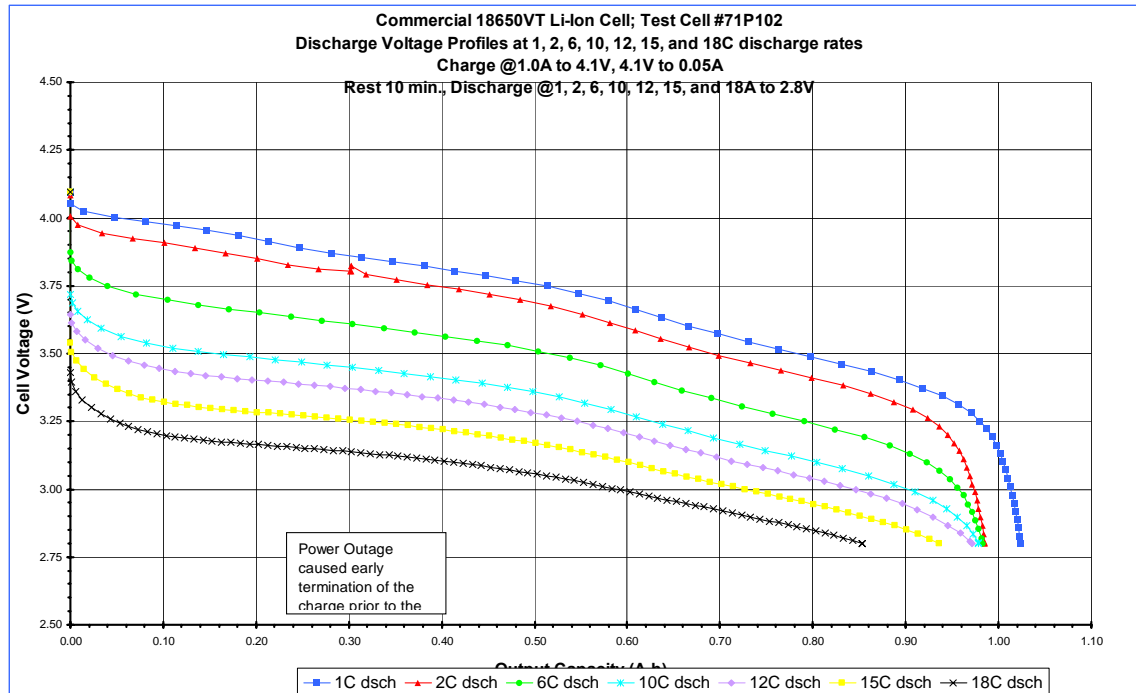



Figure 2. Discharge rate profiles for the Sony high rate cell at ambient conditions.

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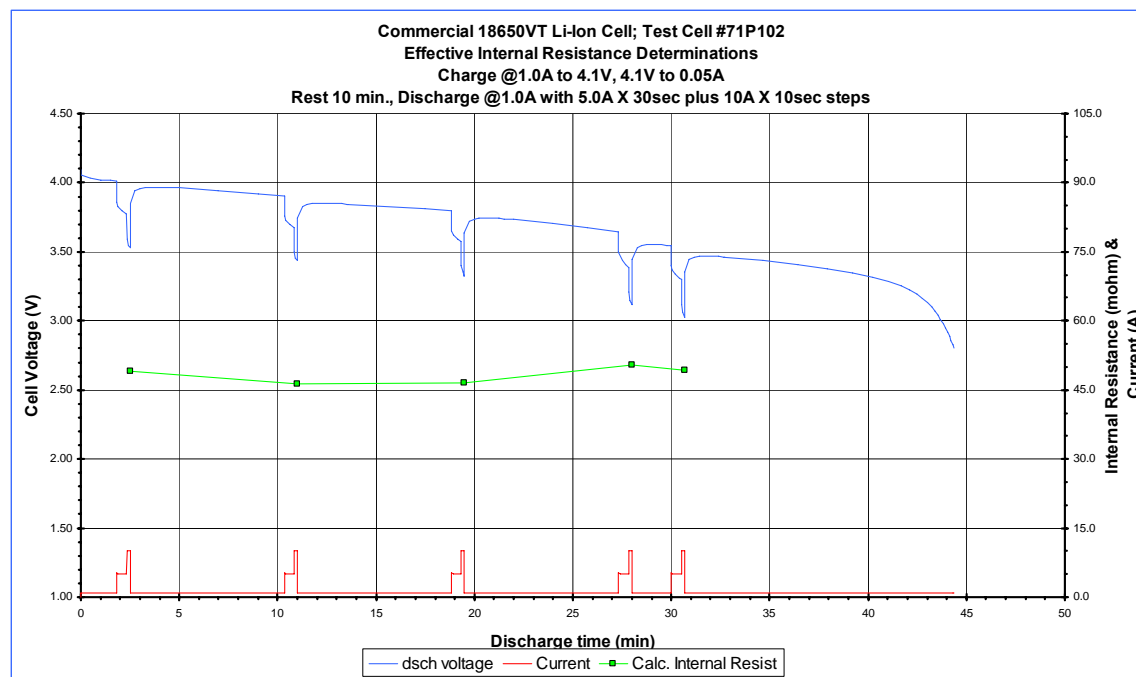



Figure 3. Internal resistance vs discharge time for the Sony high rate cell.

Two sets of CID overcharge tests were conducted, one with live cells and one with only the cell header assemblies. The live cell CID tests were conducted with the cell in connected in series with a power supply for achieving the desired compliance voltage (12 to 55V in this effort). We looked for electrical evidence of arcing during the test and physical evidence after the test. These tests were conducted at NASA-JSC.

The cell header CID test was done by Symmetry Resources using cell headers extracted from the disassembly of live cells. To be useful, the header had to be removed with at least 3 cm of can wall left and enough internal positive tab to make an electrical connection. A custom fixture was designed, fabricated, assembled, and utilized to seal the header to a gas pressure source using carbon dioxide. Special attention was paid to design of the gas supply feed to allow a slow and gradual pressure rise as we expect during moderate rate overcharge inside a cell. If the large step changes in the rise of the supplied gas pressure occurred, it could prevent any CID bounce behavior.

Once attached to the custom fixture, the cell headers were leak tested at a pressure well below CID activation pressure. Then, several headers for each cell design were pressurized to determine CID activation pressure. The cell header was load with a few drops of electrolyte (1M LiPF₆ in EC/DMC), evacuated to remove ambient air, and then backfilled with carbon dioxide to a pressure 10% lower than CID activation pressure. A current equivalent to C/2 was driven through the CID of the header assembly with a set compliance voltage (55V maximum). Carbon

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dioxide pressure was slowly (~1 psi/min) and gently increased. Current and voltage drop were recorded at a 1 MHz frequency minimum during the CID activation.

In initial test runs were done at 55V, with subsequent runs moving to 110V if no evidence of arcing was found, or 25V if evidence was found. We looked for electrical evidence of arcing during the test and physical evidence after the test. One more voltage step at 40V or 80V was planned.

Results

The pre-test acceptance results are summarized in Table 1. Note that the Panasonic design has lower internal resistance, AC impedance, and lower virgin PTC resistance.

Table 1. Pre-test Acceptance Measurements

Cell Design	OCV (V)	CCV (V)	DC Re (mΩ)	AC Imp (mΩ)	PTC Virgin Re (mΩ)	Mass (g)
Sony US18650S	3.838	3.590	124.0	64.7	22.4	40.641
Moli ICR-18650J	3.806	3.580	113.2	60.7	21.9	47.284
Sony US18650VT			46		N/A	45.359

The high rate cell's internal resistance varied from 46 to 50 mohms.

The cell design mass breakdowns from the DPAs are tabulated in Table 2.

Table 2. Cell Mass Breakdown

Component	Sony HC (g)	COTS VT (g)	Moli J (g)
Cell	40.467	41.045	47.109
Positive Insulator	0.034	0.036	0.044
PVC Sleeve	0.305	0.279	0.456
Bare cell	40.128	40.730	46.609
Electrolyte (by extraction wt. loss)	1.859	0.813	1.58, 1.14, 1.5, 0.71
Seal & Positive cover assembly	1.293	1.551	1.313
Seal	0.173	0.169	0.162
Button	0.639	1.014	0.759
PTC	0.104	NA	0.093
CID	0.218	0.215	0.189
Collector	0.120	0.116	0.110
Collector insulator	0.037	0.037	N/A

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Positive roll insulator (internal)	0.068	0.068	0.053
Negative roll insulator (internal)	0.082	0.083	0.054
Jelly roll	28.006	29.162	36.553
Positive [Al] Electrode	16.058	12.111	18.567
Negative [Cu] Electrode	9.352	13.445	12.029
Separator, 2 piece	1.547	2.032	1.562
Outside Wrap Tape	0.103	1.204	0.055
Roll Pin insert	NA	NA	1.991

*Note that electrode material flaked off during DPA, separator mass contains portions of electrode materials and electrode mass does not reconcile to jelly roll mass

The mass breakdown of all the separable components in each cell design is presented in Table 2. Note that the roll pin insert of the Moli is almost 2g and nearly 5% of cell mass.

The cross-cuts provide excellent insight into the construction of each cell header (Figs 4, 5, and 6).



Figure 4. Sony HC cell



Figure 5 Sony HR cell (no PTC)

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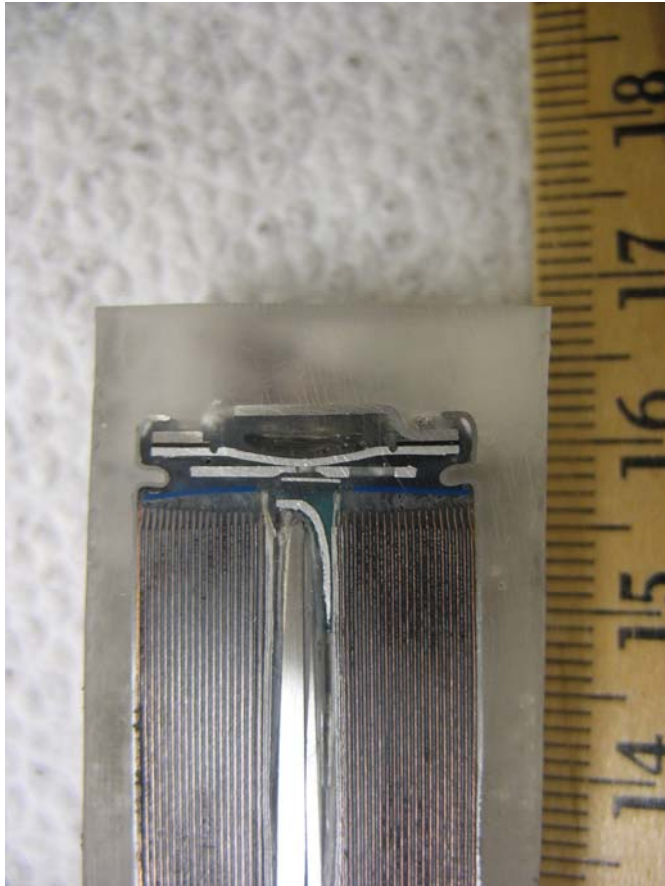


Figure 6. Moli Cell

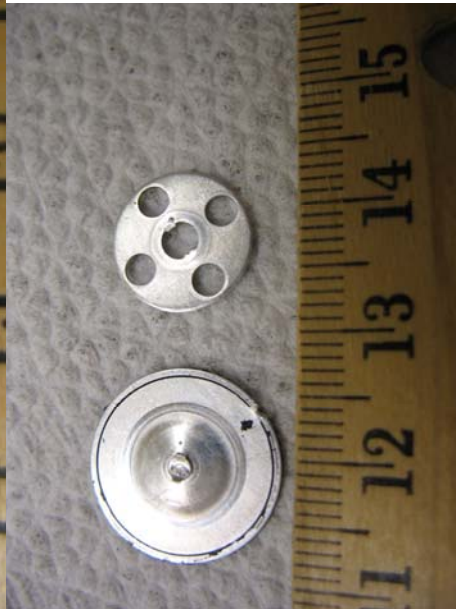


Figure 7. Moli CID and collector

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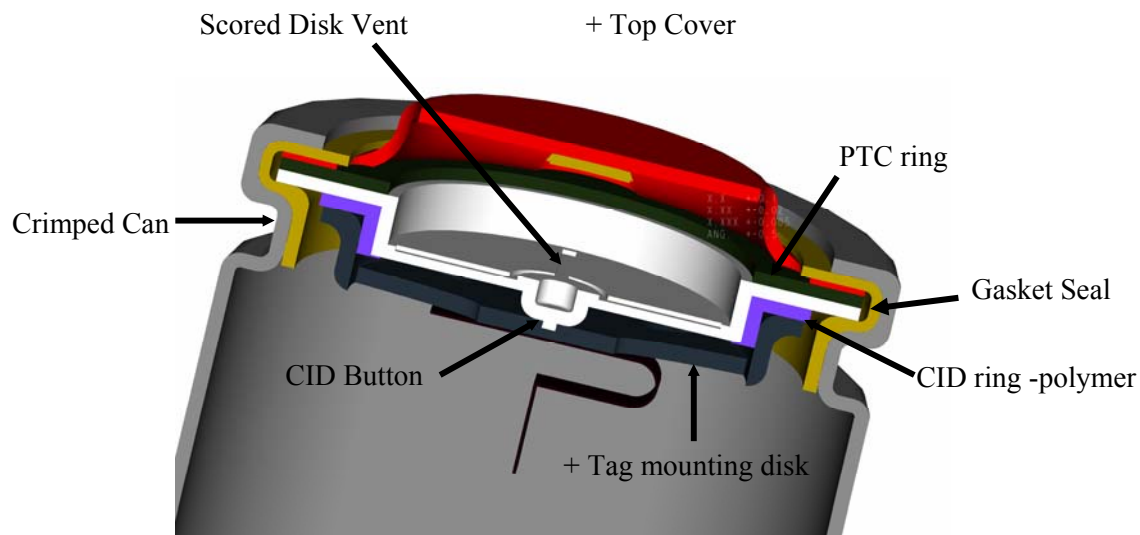
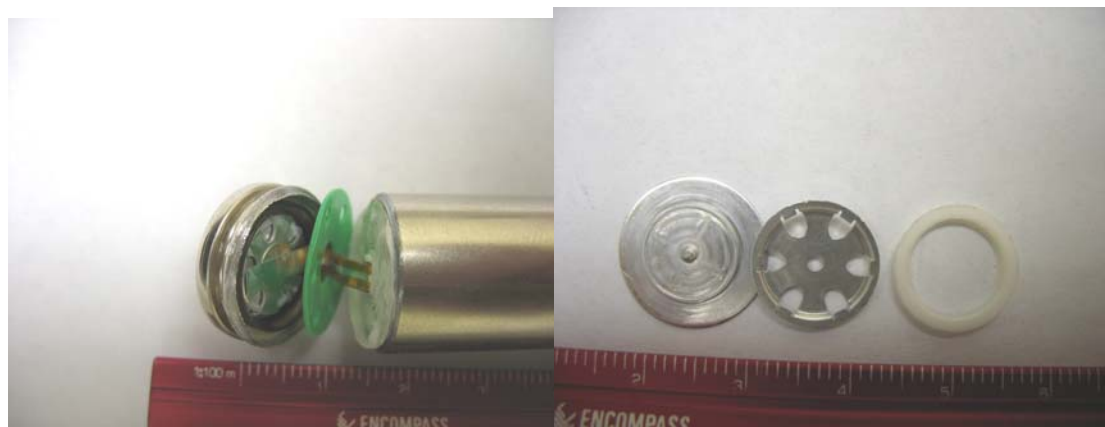



Figure 8. Model of Sony HC cell header assembly



Figures 9 & 10. Underside of Sony HC cell header assembly (left) and CID, tag mounting disk, and CID ring (right).

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Figures 11 & 12. Underside of Sony HR cell header assembly (left) and seal, button, CID, CID ring, and tag mounting disk (right).

The live cell overcharge test with the Moli cell at 12V and 55V offer an interesting comparison the physical evidence for arcing as show in Figs 13 & 14.

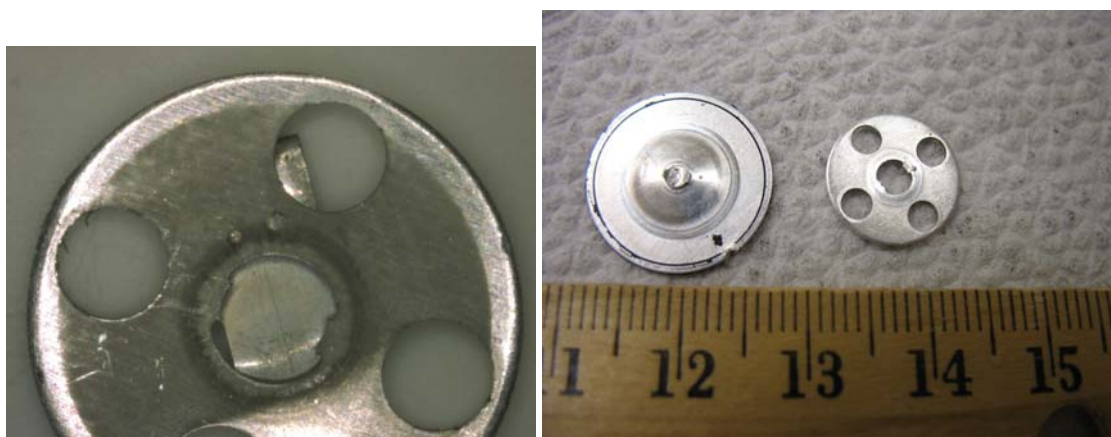


Figure 13 & 14. Tag mounting disk of Moli cell overcharged at 55V (left), while same part and CID from cell never overcharged (right)

The cell header test only arcing test yielded unquestionable physical evidence of arcing at 55V using Moli assemblies. See Figures 15 and 16.

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Fig 15 & 16. Tag mounting disk (left) and CID (right) with carbonized evidence of arcing.

The Sony HC cell did not show any evidence of arcing until tested at 110V. In Figs 17 & 18, the physical evidence is located in the CID button and the adjacent collector plate. The electrical evidence (Fig 19) is also very clear as it took over 500 ms for the CID to fully open with no more arcing.



Figure 17. CID button of the Sony HC showing clear evidence of arcing.

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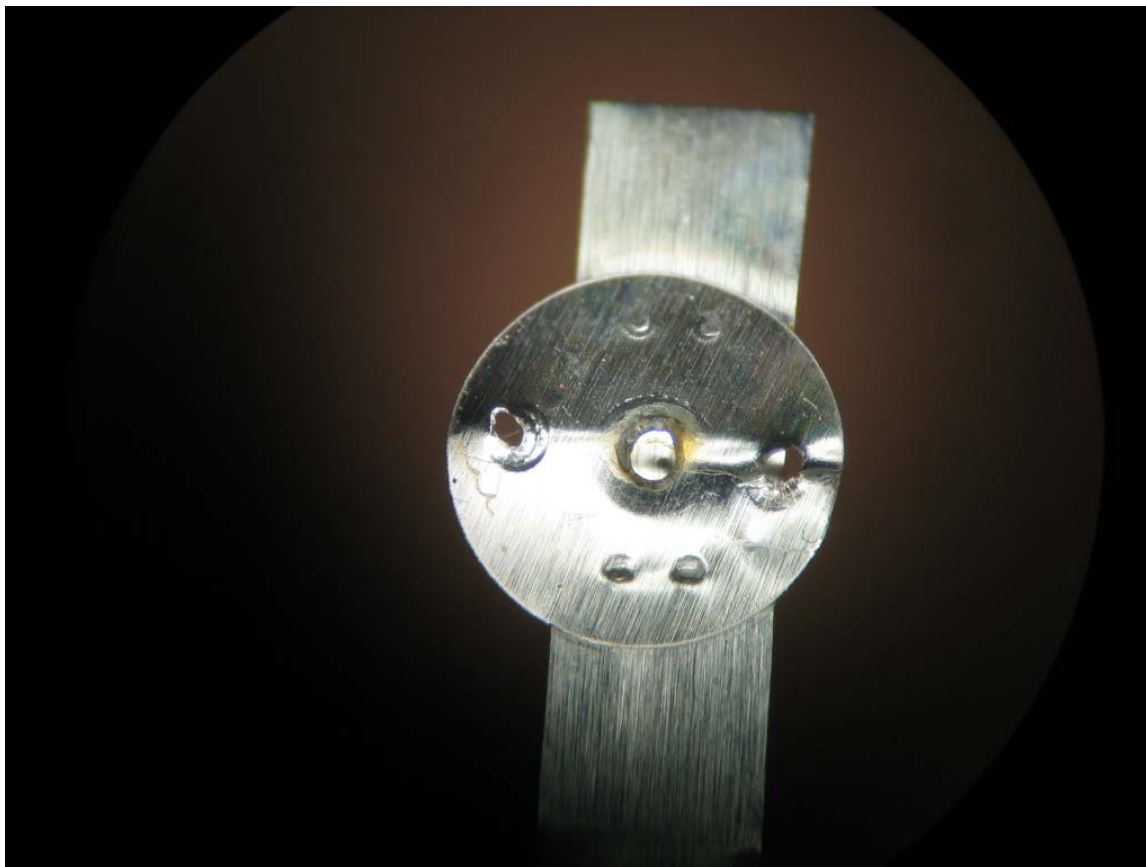
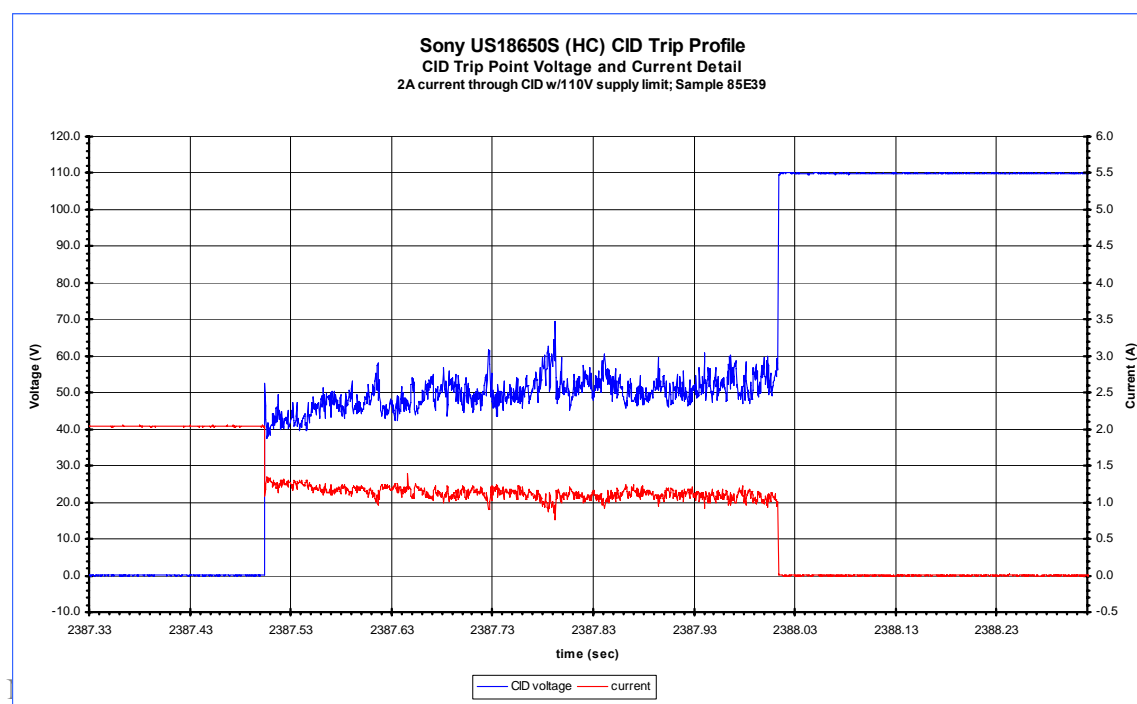


Figure 18. The opposing collector plate of the CID of the Sony cell tested at 110V.




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Figure 19. Sony HC cell header current and voltage profiles during CID activation at 2A with 110V of compliance voltage from power supply. The arcing transition last 506 ms.


Conclusions

- CID arcing can occur upon activation in high voltage conditions
 - Results are not consistently repeatable
 - Evidence for arcing noticed in only 2 of 6 Moli cells at 55V
 - Evidence for arcing noticed in only 1 of 3 Sony HC cells at 110V
 - Arcing occurred at different voltages with different designs
 - Moli ICR-18650J showed evidence at 55V but not at 37V
 - Sony 18650HC showed evidence at 110V but not at 81.5V
 - COTS high rate 18650 showed no conclusive signs of arcing even at 110V
- Confirmation runs by overcharging a Moli cell with P/S limit set at 55V
 - CID did not ignite and cause thermal runaway
 - Electrical transition of voltage and current occurred at 22V (like during header test)
 - However, transition afterwards was much slower
 - No clear evidence of arcing found upon DPA
 - Does free electrolyte act to suppress arcing?

Recommendations

- CID arcing can be controlled with these cell designs by ensuring charger power supply voltage headroom is less than 55V when charging series strings
 - Headroom = Max power supply voltage limit – Max battery voltage just prior to first CID opening
 - This will limit the voltage applied to the first CID activating and can easily be implemented

Recommend all new cell designs to be verified for arcing limits

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Appendix I. Current Interrupt Device (CID) Arcing effects in Li-Ion cells

P Patel, F. Davies, J. Jeevarajan, G. Varela, E. Darcy, G. Dorsey, and H.-T. Chu
NASA-Johnson Space Center, Houston, TX, USA

A. Test Purpose

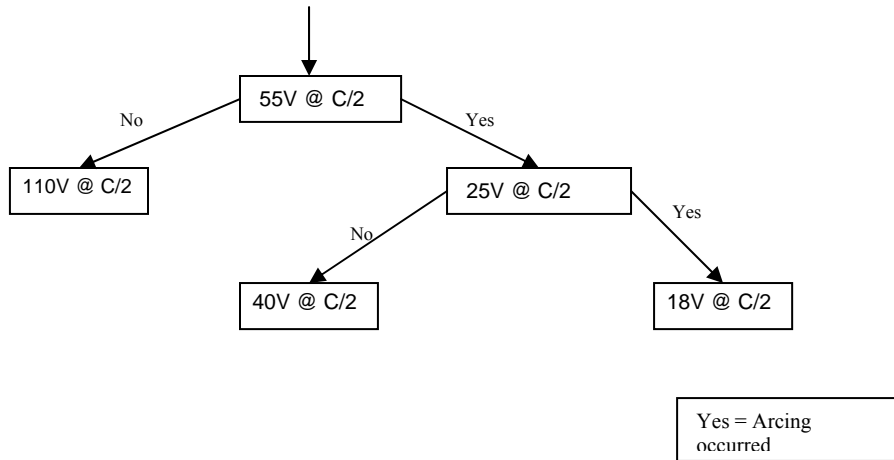
A possible source of ignition inside a cell is the CID. During CID activation, a spark could be induced due to arcing. The main questions this test will attempt to answer is if CID activation could induce arcing, whether the arcing can cause a large enough spark to ignite a flame, and whether the atmosphere where the CID activation occurs is conducive to fueling that flame.

B. Test Plan

Two methods of testing were performed: One is the CID Live Cell Test and the other is the CID Header Test. Both tests involve using three cell types: Moli (2.4Ah), Sony Hard Carbon(1.5Ah), and the COTS high rate(1.0 Ah). This report will provide the test and analysis for the CID Live Cell Test only.

The CID Live Cell Test involved overcharging a live 18650 cell until the CID activated. This test was performed with various voltage limits ranging from 18V to 110V to determine an approximate range where arcing occurred. The test started at the middle of the spectrum with charging at 55V with a C/2 rate and stepped to a higher voltage if arcing was not observed or to a lower voltage if possible arcing was observed (See Table 1). The current and voltage curves are monitored throughout the duration of the test at a 1 Hz sampling rate. When the CID activated, data was collected at a MHz rate to capture the minor fluctuations during activation. The cells were then taken for Destructive Physical Analysis (DPA) and high magnification imaging to look for physical signs of arcing.

Moli 18650 / Sony Hard Carbon 18650 / COTS Hi-Rate 18650



C. Results

For the CID Live cell test, instead of the expected smooth current drop when the CID activates (Figure 1), we see irregular voltage and current curves while charging at 55V (Figure 2, 3 and 4). The DPA of these cells show discoloration on the bottom portion of the CID (Figures 5 – 9). However, there is no conclusive evidence of arcing.

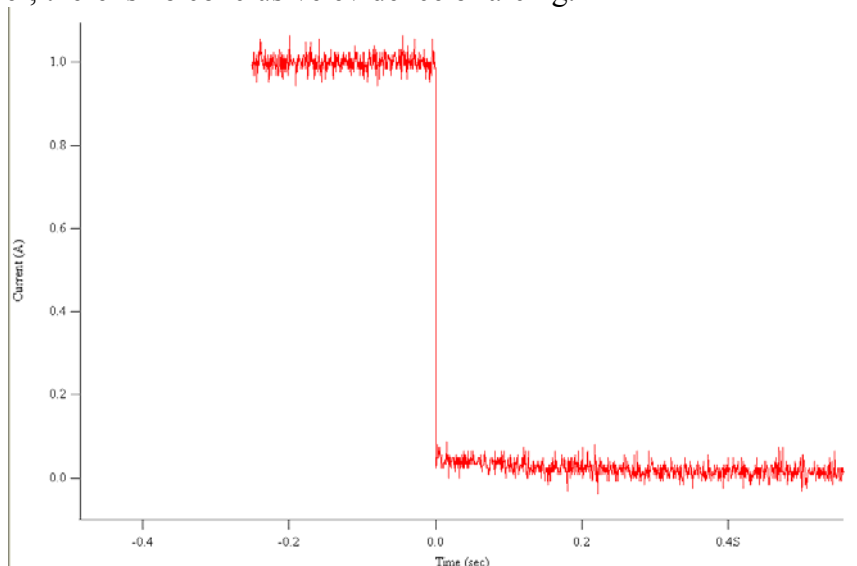


Figure 1: Moli Live Cell CID activation (12V - 1.2A charge)

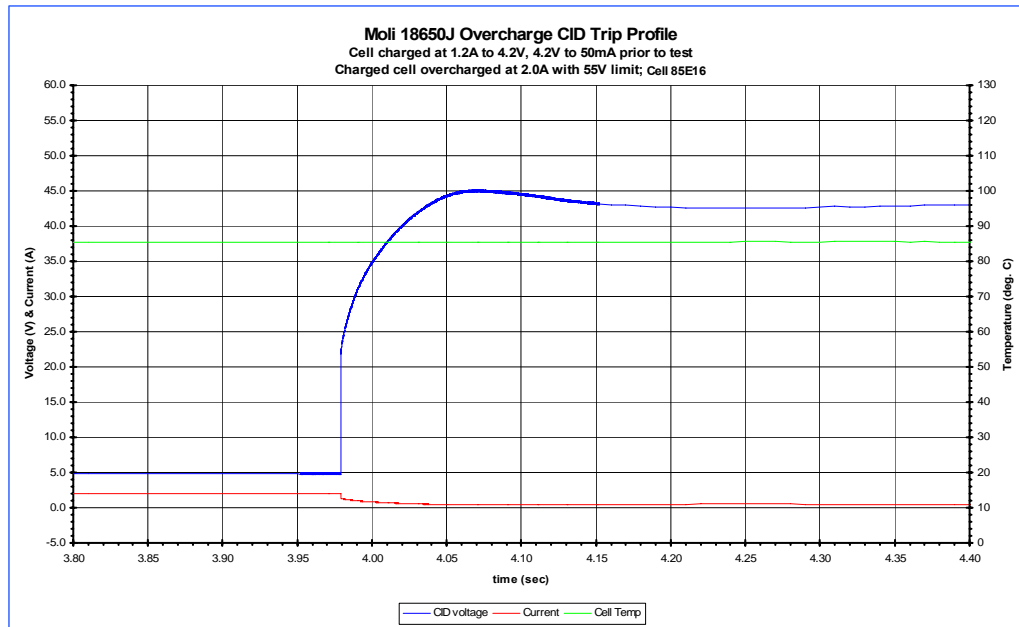


Figure 2: Moli Live Cell CID activation (55V - 1.2A charge)

Moli 55V Voltage Profile

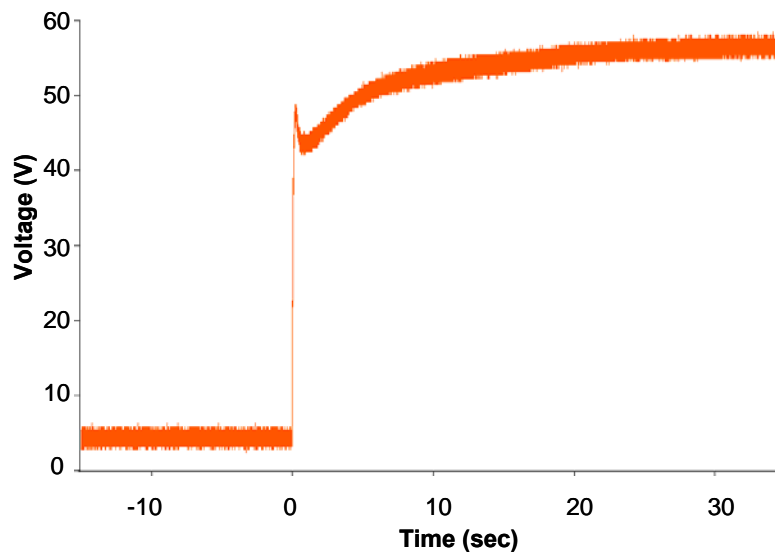
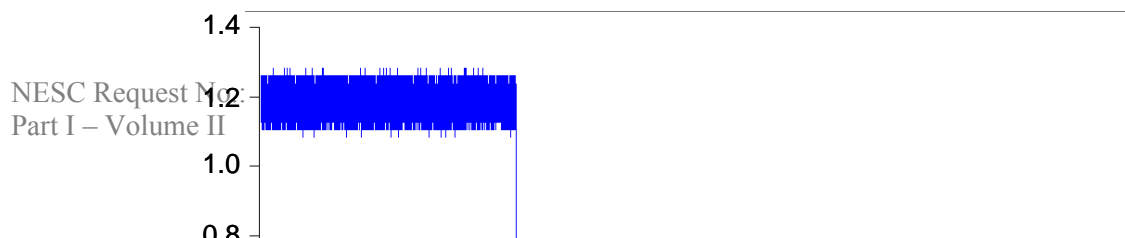


Figure 3. Voltage Profile for the Moli Live Cell CID Activation Test with a voltage of 55 V.

Moli 55V Current Profile




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Figure 4. Current Profile for CID Test at 55 V for the Moli Cell.



Figure 5: Bottom portion of CID (55V)



Figure 6: Bottom portion of CID (12V)

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Figure 7: Bottom portion of CID Enlarged (55V)

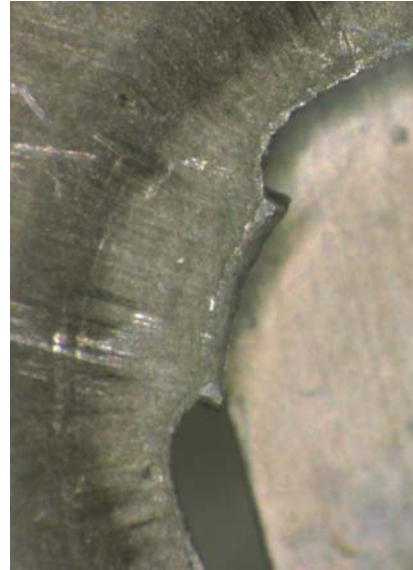



Figure 8: Close up of contact



Figure 9: Bottom portion of CID Enlarged (12V)

The CID discs were then analyzed for the chemical composition of the discoloration found on them by using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Two specific areas of the disc that were studied were the inner and the outer sections of the disc. The micrographs were compared to the composition of a CID disc that was fresh and not subjected to any test. The SEM and EDS images are provided in Figures 10 to 12 for the discolored CID sections as well as a fresh CID. Traces of phosphorous were identified in the

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inner areas of the discolored discs and in addition to this, traces of chlorine were also identified in the outer areas of the discs. The cell seals were then analyzed used the same technique and it was determined that the seals had large traces of chlorine. Figure 13 gives the SEM and EDS for the cell seals.

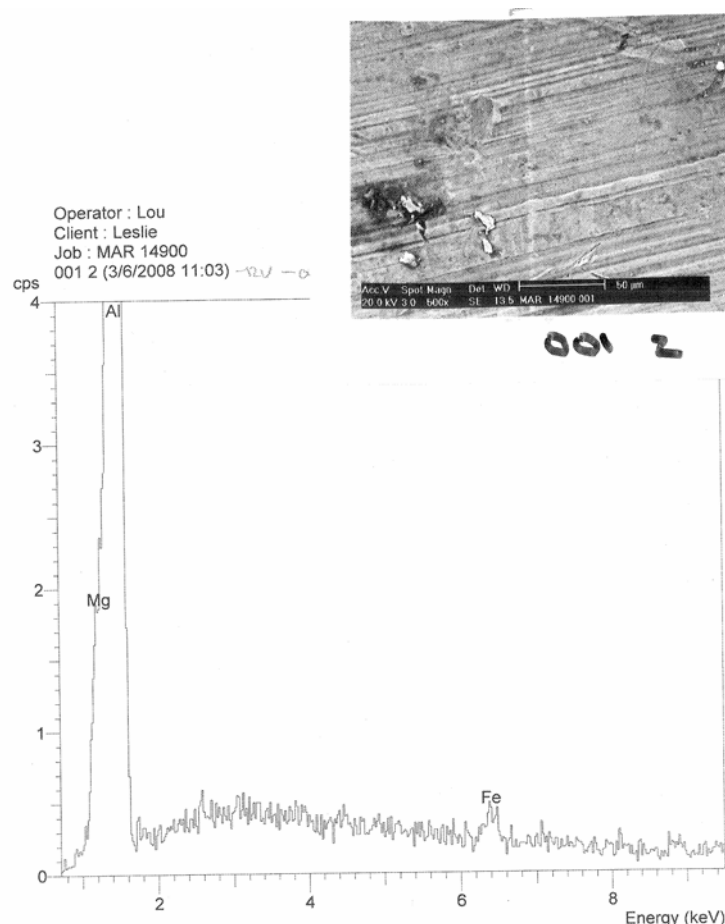



Figure 10. SEM and EDS of CID Disc from a fresh cell.

In summary, although CID arcing is expected when the CID opens (under pressure) in the presence of high voltages, it may not be as marked, due to the dampening of this event by the electrolyte vapors and liquid that wet it during the process. When the pressure inside the cells increases and pushes the CID disc, some hot electrolyte liquid and vapors may also splash onto the CID discs. Although this may dampen the arcing effect, it may cause other catastrophic hazards to occur in a string or bank configuration due to the heat build up in the cell and due to the heat transfer occurring through the tabs in the string or bank. Cell seal softening was also observed and confirmed by elemental analysis. Hence, although there was no confirmed arcing for the full-cell samples tested for the Moli cells, exposure of the CID to high voltages during its opening can cause catastrophic hazards.

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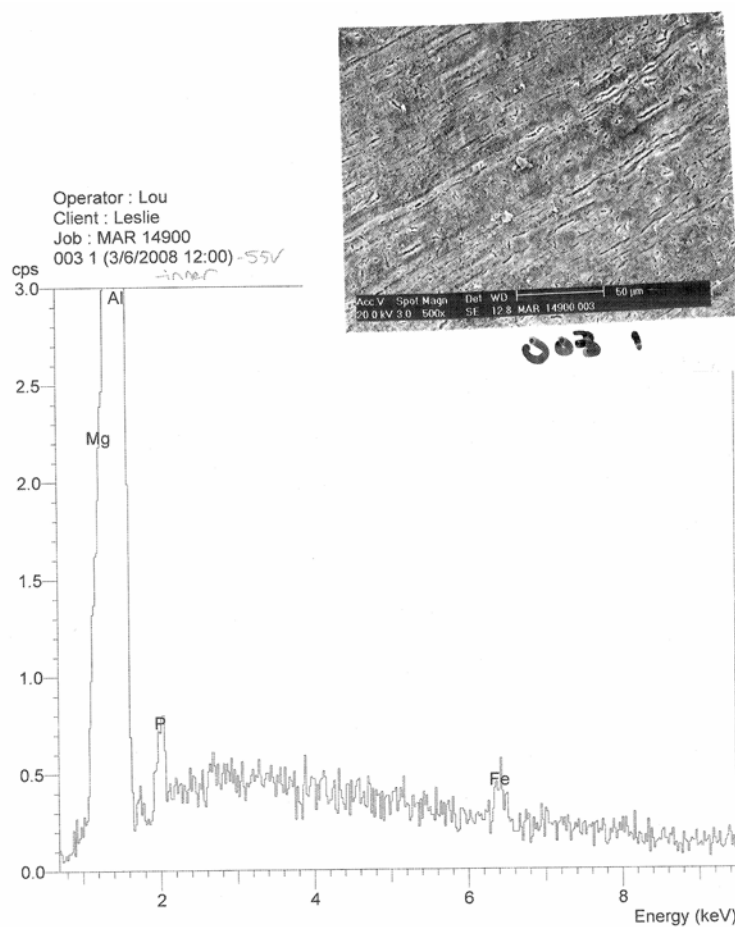



Figure 11. SEM and EDS spectrum for the Composition of the Discoloration found on the inner portion of the CID disc.

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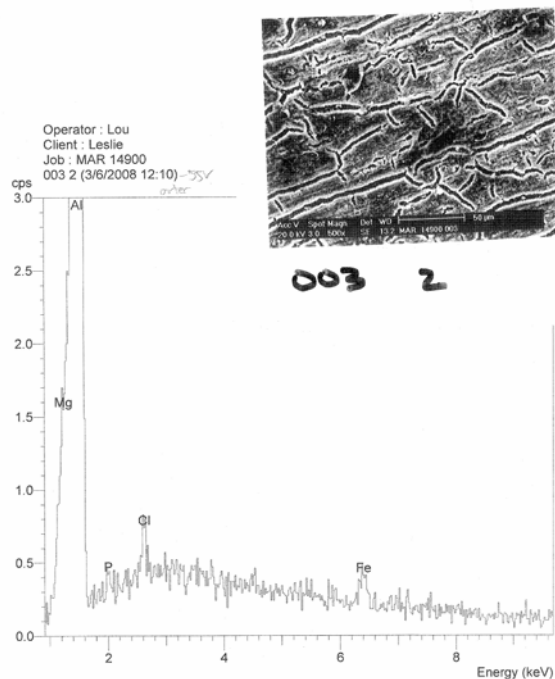


Figure 12. SEM and EDS spectrum for the Composition of the Discoloration found on the outer portion of the CID disc.

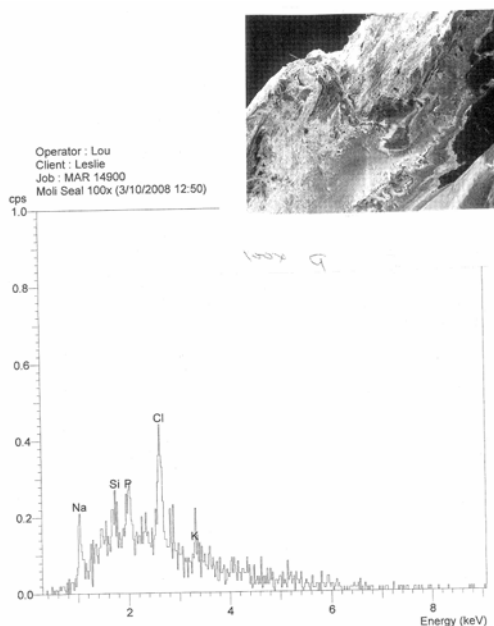



Figure 13. SEM and EDS spectrum for the Seal material found in the Moli 18650 cell

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Appendix J. Series String and Parallel Bank External Short and Overcharge Test Report

J. Jeevarajan, F. Davies, P. Patel, G. Varela and E. Darcy
NASA-Johnson Space Center, Houston, TX, USA


R. Shah, C. Keen, C. Weitzel (Mobile Power Solutions)
W. Tracinski (Applied Power International)

Background

The PTC has voltage limitations and when activated under high voltage conditions, can spontaneously ignite. Under overcharge conditions, at voltages above 4.5 V, electrochemical decomposition of the organic electrolyte occurs producing large quantities of carbon monoxide that gets converted to carbon dioxide with continued voltage increase. In the 18650 cell design, an internally located Current Interrupt Device (CID), which opens under pressure and is typically non-resettable, causes the cell to remain open (unusable) after activation. Observations of the CID not being protective in high voltage cell strings led to testing of the single, four cell and fourteen cell series strings under overcharge conditions (Ref. 6 and 7). The CID activated in all single cells above 5.0 V, although the time it took for the CID activation varied from cell to cell. In the four cell string, the string becomes inactive after the CID in one cell activates resulting in a high resistance in the string. In the fourteen cell string, a close analysis of the oscilloscope data as well as the high speed data, indicated that the first CID activation was incomplete. In this test, a current spike of 2.5A was observed that then lowered to about 1.6A and oscillated between 1.6 and 1.5 A for a period of about 35 seconds, after which it fell to 0 A. During this period, a second cell spiked to about 24 V and fell to about 8 V. For the next 200 seconds, the voltages of at least two cells increased, but remained below 10 V, even though the current to the cell string was at 0 A. Soon after this, thermal runaway resulted. Some of the details of the test data are provided here to bring out the fact that communication between the cells, was observed, although the high resistance at the total string did not allow any charging currents. A closer look at the cell voltages indicated that at least three cells dropped in voltage below 0 V, indicating PTC failures. The probable causes of increased vapor pressure of the hot flammable electrolytes, the presence of oxygen released from the cathode at high voltages, and the presence of the PTC ignition source resulted in the cells venting, disassembly, violent reactions and thermal runaway. Another possibility is the creation of sharp edges during the opening of the CID that could cause the incidence of an arc in the presence of hot flammable gases.

Tests

Although the results of the short circuit test were not unexpected, the results of the overcharge test were and this led to further study of these cylindrical cells and their internal safety components. Although cells from different manufacturers, such as Sony, Moli, Panasonic and

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Sanyo were purchased, this particular set of tests was carried out on the Sony 18650 hard carbon cells only. Overcharge and external short tests were performed on single cells and on different lengths of strings and banks.


External short and overcharge tests on cells in series or parallel configurations:

The test was performed with Sony 18650 cells of 1.5 Ah capacity. The cells were at first removed from Canon camcorder batteries. However, initial tests indicated that the cells had been compromised during the removal from the packs and the results were more catastrophic in nature. After these observations, fresh single cells that had been purchased directly from a battery company were used for the tests. Cells were tested as single cells, bank of four cells and bank of 16 cells. For these combinations, the limits were varied to determine the tolerance as well as the limitations of the protective devices. All string and bank configurations had cells arranged in a single row (fence-post) type and laid flat as shown in the figures. Changes were made during the test program to get the best results possible from the test program.

A summary of the results is provided in the Table 1, below. The test samples were cells removed from a Canon camcorder battery pack of known heritage and fresh cells. All the 16P tests were carried out with fresh cells. Of the 4P tests only the 12 V, 6A that did not experience a thermal runaway was performed with the fresh cells. The external shorts on the series strings were all carried out on cells extracted from the Canon battery packs.

Table 1. Summary of overcharge and external short tests carried out on Different Module Configurations with Different Voltage and Current Limits

Description	Volts	Amps	Load (Ohms)	Notes
Single cell overcharge, 2X	12	1.5		CID operates; Canon / fresh
4P overcharge, 48V, 6A	48	6		Thermal runaway; Canon
4P overcharge, 12V, 6A	12	6		CID operates; fresh
4P overcharge, 12V, 6A	12	6		Thermal runaway / Canon
4P overcharge, 12V, 4A	12	4		CID operates / Canon
16P overcharge, 48V, 24A	48	24		Thermal runaway / fresh
16P overcharge, 12V, 24A	12	24		Thermal runaway / fresh
16P overcharge, 12V, 12A	12	12	2	CID operates /fresh
16 P external short				No thermal runaway /Canon
Single Cell external shorts				No failures; PTC trips / Canon

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4S External short			50 No failures; PTC trips / Canon
14S External short			50 PTC fails; venting and sparks / Canon
4S Overcharge	48	1.5	No failure; CID activates / Canon
14S Overcharge	84	1.5	Thermal runaway / Canon

Results and Observations

In all cases, the single cell overcharge and external short tests had expected results with CID opening and PTC activation occurring without any catastrophic failures.

The 4P overcharge test with 6A current (equivalent to 1C rate per cell) and 48 V limit, had the following results (Figure 1). The current on Cell #4 dropped to approximately 200 mA at about 1 hour into the overcharge condition. Two minutes after this occurred, the CIDs tripped on cell 1, cell 2 and cell 3 sequentially. At this point, cell #4 was carrying all the current (6A) and explosive venting with flame and thermal runaway occurred. The cell can showed splitting (Figure 2). The maximum temperature recorded on this cell was only 51 °C just before the venting occurred.

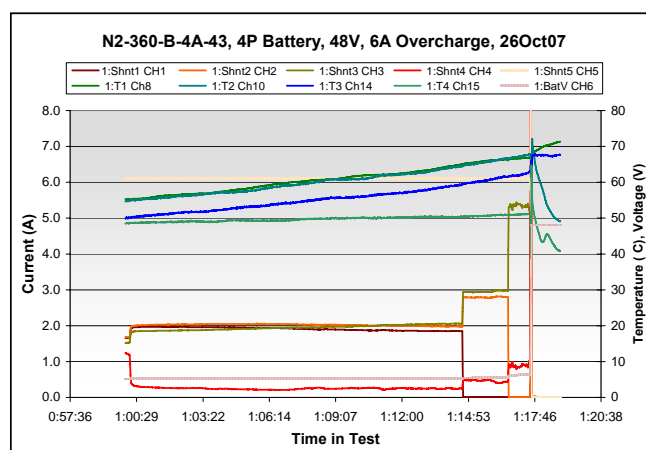


Figure 1. Overcharge test on 4P bank of Sony Li-Ion cells using 6A current with a 48 V limit.


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Figure 2: Cell #4 after the 4P overcharge test with 6A and 48 V limit.

Figure 3 provides a chart for the results observed during the overcharge of the Sony li-ion cells (removed from the Canon battery packs) in a 4P configuration were subjected to the 6A, 12 V limit. At ~45 minutes into the charge, cells 1 and 2 went to a low current leaving 3 and 4 to carry more current; at ~48 minutes, cells 3 and 4 returned to carrying high current, and all 4 cells evened out at ~49.5 minutes; at 54 minutes cell 3 appeared to activate its CID followed by the other 3 cells over the next minute; at 54:52, cell 3 jumped from 109° C to 120° C in less than 1 second with runaway to >500°C; each of the other 3 cells vented flame as well, probably due to thermal propagation of the initial event. When the test was repeated with fresh Sony li-ion cells obtained from a cell vendor, all cells had their CIDs activated as expected. Figure 4 gives the results obtained.

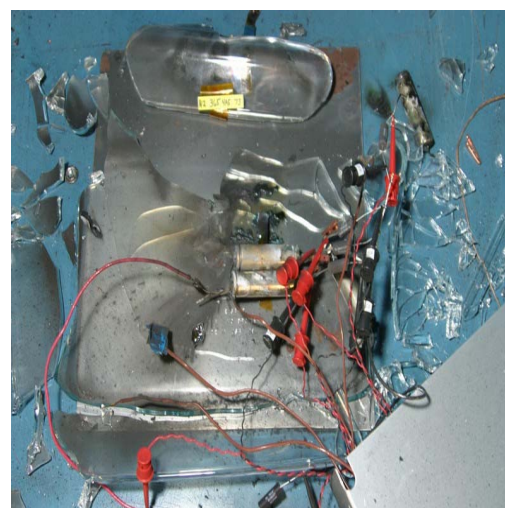
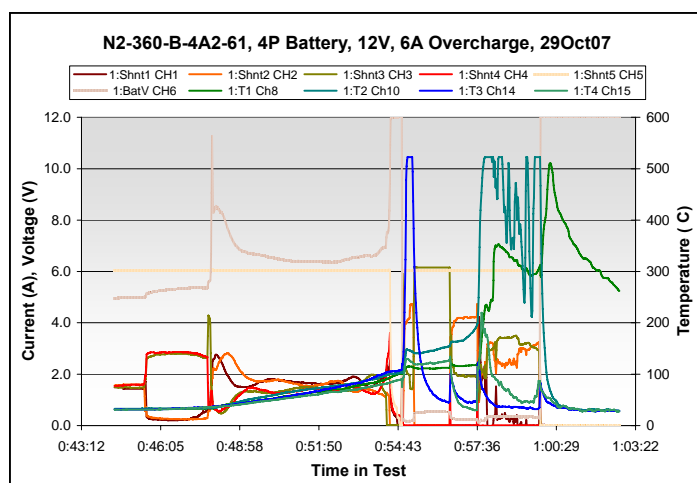



Figure 3. Overcharge test on 4P bank of Sony Li-ion cells (from Canon pack) with 6A and 12 V limit. A photo of the broken pyrex dish is shown on the right.

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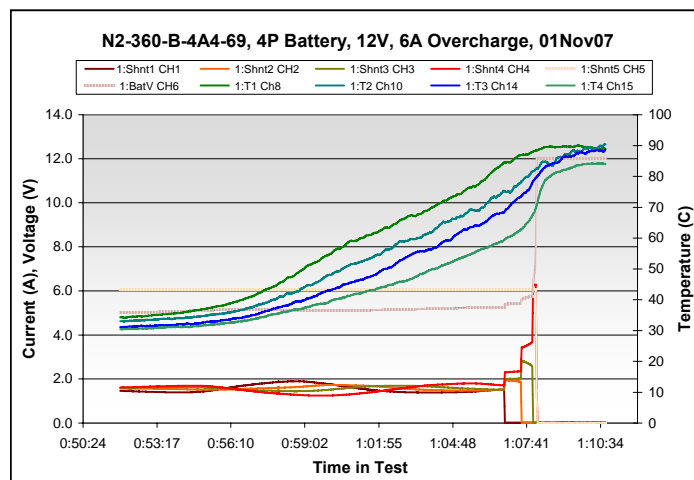


Figure 4. Overcharge test on 4P bank of Sony Li-ion cells (fresh cells) with 6A and 12 V limit.

The 4P overcharge test with 6 A and 12 V was repeated on the Sony cells from the Canon packs and the same catastrophic results were obtained. Cells from the batch were analyzed and found to have been compromised (ac impedance was much higher compared to fresh cells). Hence further investigation was carried out to measure PTC resistances and ac impedance of the cell. The cell voltage and ac impedance and PTC resistances are given below:


Cell 1: OCV: 4.062V, AC imp.: 80.7mohm AC, PTC resistance: 30.9mohm
Cell 2: OCV: 4.051V, AC imp.: 67.2mohm AC, PTC resistance: 21.2mohm
Cell 3: OCV: 4.033V, AC imp.: 86.2mohm AC, PTC resistance: 26.7mohm

The fresh Sony 18650S cells had an average AC impedance of 64.7mohm with a range of 62.2 to 68.2mohm. The PTC resistance was 22.4mohm average with a range of 21.1 to 24.1mohm. Cells 1 and 3 above, seem to have been adversely affected during or after pack disassembly. The elevated PTC resistances are consistent with recovered values on a tripped PTC.


A second set of Canon batteries were opened up with more care and the ac impedances and PTC resistances of the four cells were measured. The values were more in the range for fresh cells as provided below:

OCV: 3.511, 3.512, 3.500, 3.500 volts
AC Imp.: 88.8, 88.3, 89.1, 91.0 milliohms
PTC resistance: 24.4, 24.0, 25.1, 24.9 milliohms.

This data indicated that the cells from the Canon packs that underwent the 4P test with 12 V and 6A limits had been compromised while they were being removed from the packs.

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The last set of tests on the 4P bank was an overcharge with 4A and a 12 V limit. This test also activated the CIDs without any catastrophic failures. Figure 5 gives a plot of the current, voltage and temperature for this test. It was observed that the current going into one cell drops to a low value (possible PTC activation) while the others accept more current. Cell 1 has its CID activated first and then cell 2, followed by that for cell 4 and finally the CID for cell 3 activates shutting off current going in to bank. It was observed that the current is constantly being shared and balanced by the cells. The test was repeated under the same conditions and the same results were observed.

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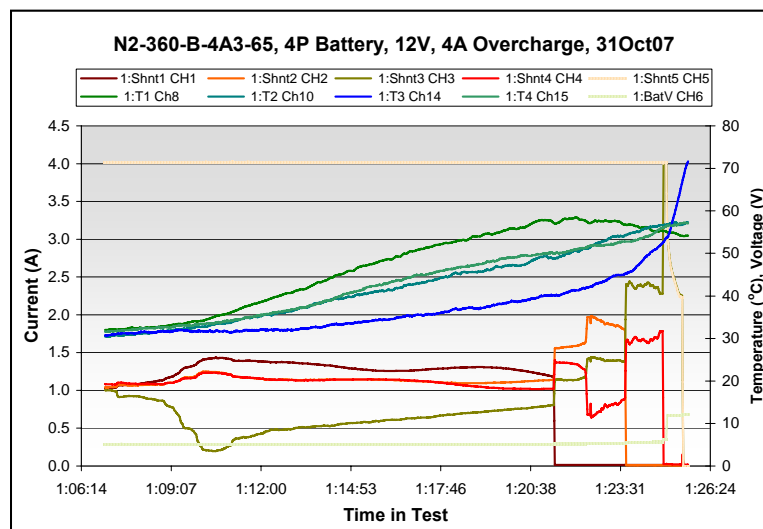
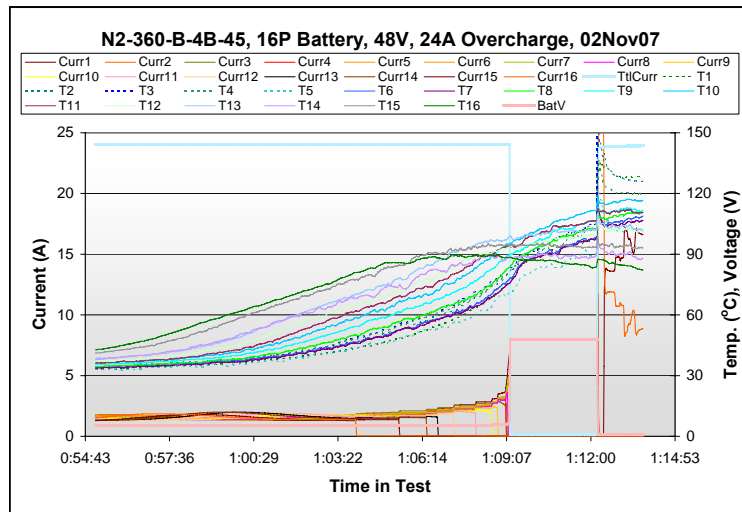


Figure 5. Overcharge test on a 4P bank of cells at 4A with a 12 V limit.

The next set of tests was carried out on 16 parallel cells. The first test with this configuration was an overcharge test with 24A and a 48 V limit. It was observed (as shown in Figure 6a) that the CIDs activated in succession for about half the number of cells. At this point, the temperatures on several of the cells show steady increase and then there is a sudden thermal runaway as the last few CIDs try to open at the same time.

It was observed that cell 3 was at 84 °C when its CID activated but it reached about 106 °C within about 3 minutes and went into a thermal runaway (Figure 6 b). Even after the current fell to 0 A, the cell temperatures continued to rise until thermal runaway occurred. The thermal runaway could have been caused by the ignition of a high-resistance PTC (activated due to high temperature) that was exposed to the high voltage (48V limit on power supply). Although 13 of the 16 cells were intact, most of them did not have good cell voltages as seen in Table 2.



(a)



(b)

Figure 6: Overcharge Test on a 16P configuration with a current of 24A and a voltage limit of 48 V.

Table 2. Cell Voltages and AC impedance for the Cells Subjected to a Charge current of 24 A and a voltage of 48 V.

	Post Test OCV (V)	Post Test 1kHz ACZ (Ohm)
N2-360-B-4B-45		
N2-360-B-4B-46		
N2-360-B-4B-47		
N2-360-B-4B-48	0	0.00514
N2-360-B-4B-49	2.3043	753
N2-360-B-4B-50	1.5927	1294
N2-360-B-4B-51	1.9744	2186
N2-360-B-4B-52	0.3707	1166
N2-360-B-4B-53	0.5037	641
N2-360-B-4B-54	0.3444	1798
N2-360-B-4B-55	1.1678	667
N2-360-B-4B-56	0.3407	3654
N2-360-B-4B-57	0.3454	2387
N2-360-B-4B-58	1.0635	13952
N2-360-B-4B-59	0.9018	17433
N2-360-B-4B-60	0.9345	17533

The next test was an overcharge test carried out on a 16P configuration with a 24 A charge current and 12 V as the voltage limit. This test also resulted in catastrophic thermal runaway that

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was worse than the above test. The CIDs tripped in succession (Figure 7) and two minutes after the last cell had its CID tripped, one cell in the middle of the bank (cell 8) vented sparks and flame. This was immediately followed by venting and burning of the cells on either side (cells 7, 9, 10 and 11) of it. After this, all the cells went into a thermal runaway with the cells that initiated the event being expelled from the cell bank.

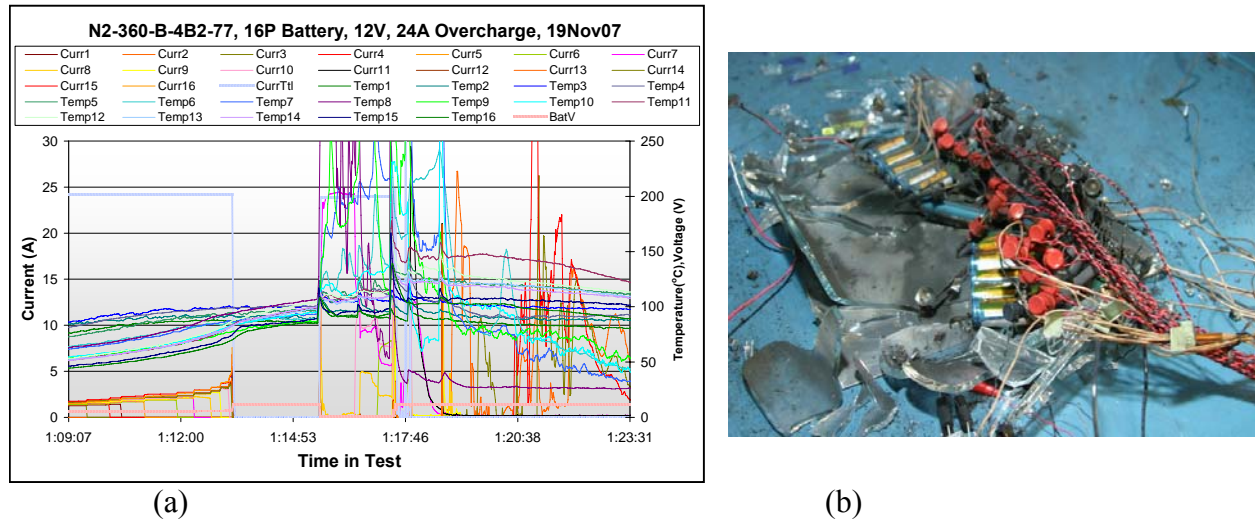
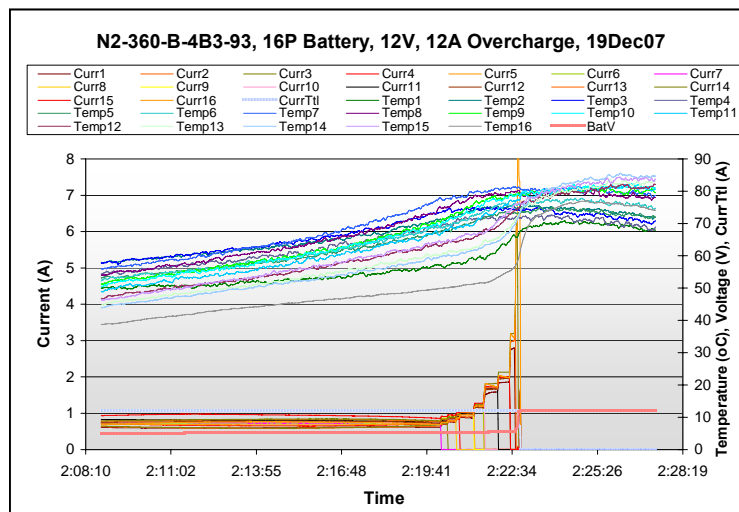


Figure 7. Overcharge Test on a 16P bank with a current of 24A and a voltage limit of 12 V.

The third set of tests included the same 16P configuration of cells that were overcharged with a 12 A current and 12 V limit. The CIDs in the cells activated with no catastrophic failures. Figure 8 depicts the data indicating CID openings in all the cells with no thermal runaway. The voltages on all the cells were measured and although it appeared that the cells had some voltage, these values dropped as soon as a load was placed on them. The AC impedance values in Table 3 indicate that the cell impedances were extremely high indicating opening of the CIDs as expected.



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Figure 8. Overcharge Test on a 16P bank with a current of 12A and a voltage limit of 12 V.

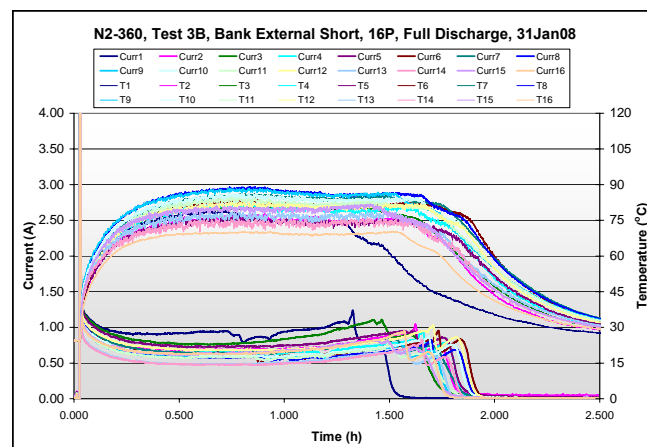
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Table 3: Voltage and AC impedance values for the cells in the 16P overcharge Test with 12 A and 12 V limit.

	Post Test OCV (V)	Post Test 1kHz ACZ (Ohm)*
N2-360-B-4B3-93	2.192	200000
N2-360-B-4B3-94	1.685	300000
N2-360-B-4B3-95	1.960	230000
N2-360-B-4B3-96	2.156	151000
N2-360-B-4B3-97	2.010	250000
N2-360-B-4B3-98	2.200	240000
N2-360-B-4B3-99	2.065	17300
N2-360-B-4B3-100	2.096	210000
N2-360-B-4B3-101	1.983	5100
N2-360-B-4B3-102	2.237	1300
N2-360-B-4B3-103	1.828	60000
N2-360-B-4B3-104	2.223	8100
N2-360-B-4B3-105	1.701	9100
N2-360-B-4B3-106	1.633	32000
N2-360-B-4B3-107	1.627	7800
N2-360-B-4B3-108	1.936	3000

*rounded to nearest 100 Ohms

Finally, an external short circuit test was carried out on a 16P bank of cells with a load of 2 mohms. No catastrophic failures were observed. The maximum temperature recorded was 89 °C (Figure 9) and the total peak current observed was 361 A (Figure 10). The voltage drops to 1.48 V at short initiation which then falls to around 0.41 V about 3 seconds into the shorting process and it tapers to less than 100 mV after 2 minutes into the whole process. The voltage then settles down to between 50 and 60 mV until the last cell is fully discharged at which point the voltage falls to 0 V.




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Figure 9: External short circuit test on 16P configuration with 2 mohms.

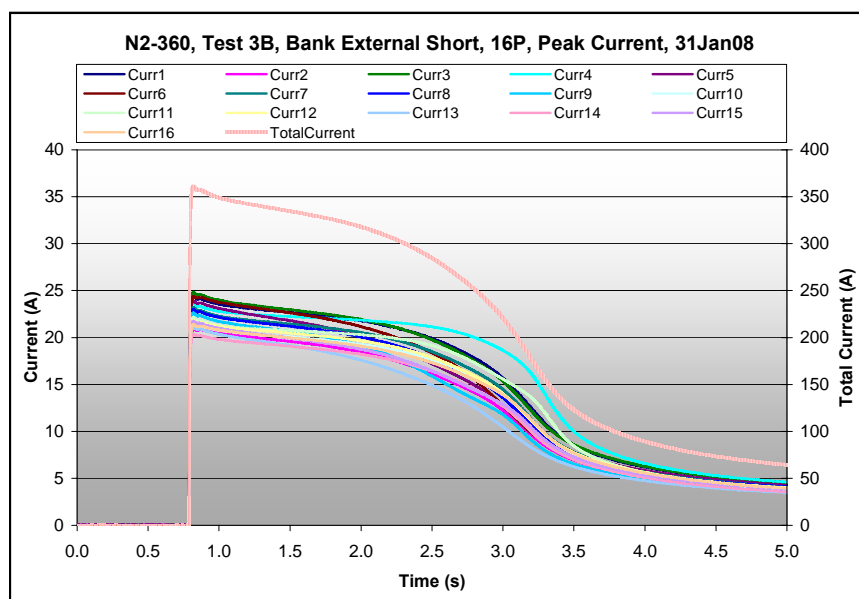


Figure 10. Peak Currents observed Under the External Short Conditions for the 16P test.

For completeness, results of the tests carried out on a test program just before this one will be provided below (as mentioned at the beginning of this section). This set of tests consisted of cells in series. The single cell and 4S (four cells in series) tests under overcharge and external short conditions performed as expected. The results of the 4S external short and overcharge tests are given in Figures 11 and 12. Under the external short test, one cell PTC gets activated and remains in that condition until the load is removed. The maximum temperature recorded was 75 °C. When the 4S cells were subjected to the overcharge conditions, one cell CID trips safing the string. The maximum temperature recorded was 83 °C. The tests carried out on the 16S strings were not as benign. The 16S external short tests (Figure 13) resulted in several cells undergoing rapid venting within the first ten seconds with sparks and charring of the header. Due the exposure of the PTC to very high voltages (above its threshold voltage), the results of the test are catastrophic.

During the overcharge test on the 16S string (Figure 14), a current spike of 2.5A was observed that then lowered to about 1.6A and oscillated between 1.6 and 1.5 A for a period of about 35 seconds, after which it fell to 0 A. During this period, a second one spiked to about 24 V and fell to about 8 V. For the next 200 seconds, the voltages of at least two cells increased, but remained below 10 V, even though the current to the cell string was at 0 A (Figures 15 and 16). After this, the current into the string is cutoff, but the cells share current and the voltages undergo so many changes until finally two cells go into thermal runaway. Analysis of the oscilloscope data

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indicated that some cells went into negative voltages indicating PTC failures. The heat buildup in the cells could have caused the PTC to trip in some cells which are then exposed to the high voltage string of greater than 50V, causing thermal runaway and catastrophic failures. Two cells were completely ejected from the string and two were dangling from the test table.

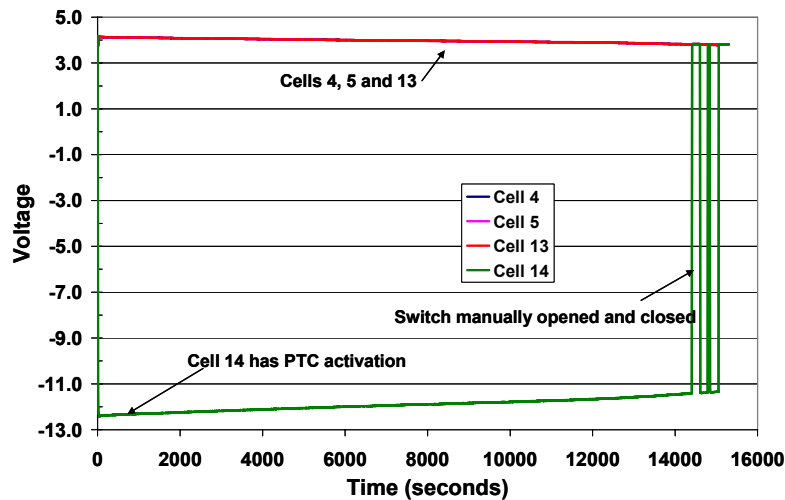


Figure 11. External Short Circuit test on 4S set of cells with a load of 50 mohm.

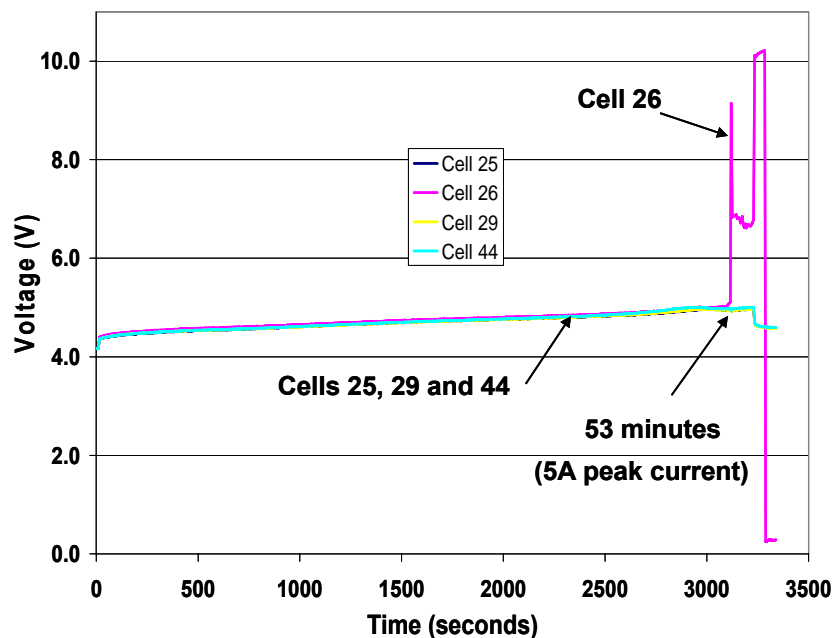



Figure 12. Overcharge Test on 4S set of cells with 1.5A current.

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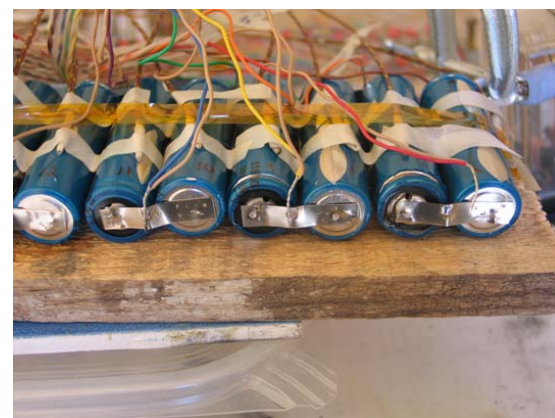
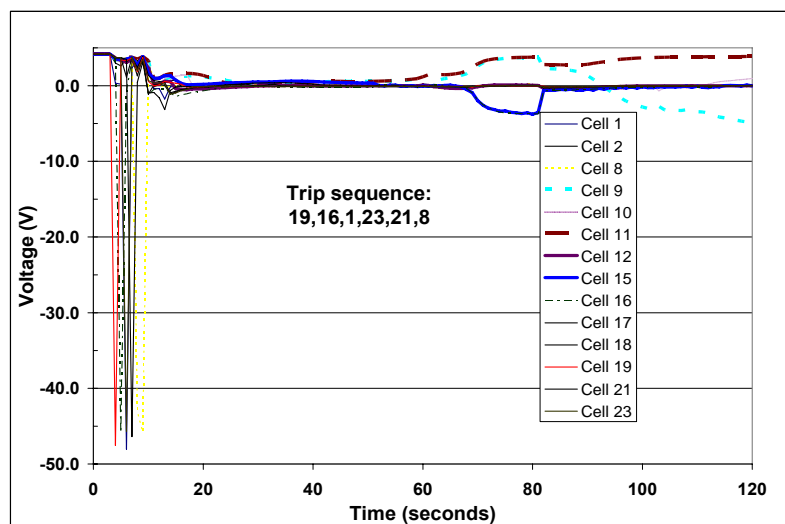
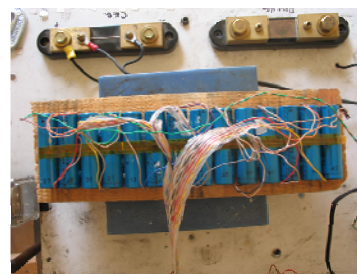
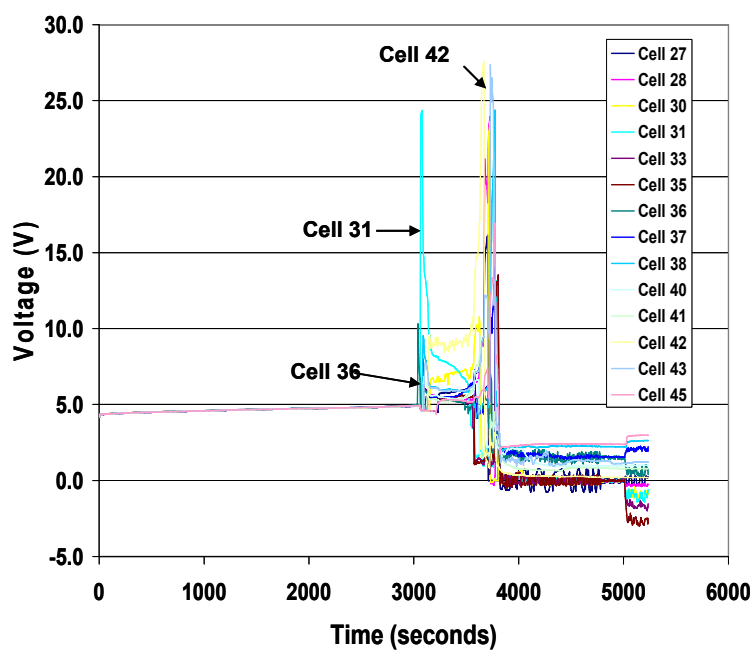


Figure 13. External Short Circuit Test on 14S set of cells with 50 mohm load.




Cells before Test



Cells After Test

Figure 14. Overcharge Test on 14S set of cells using a current 1.5 A.

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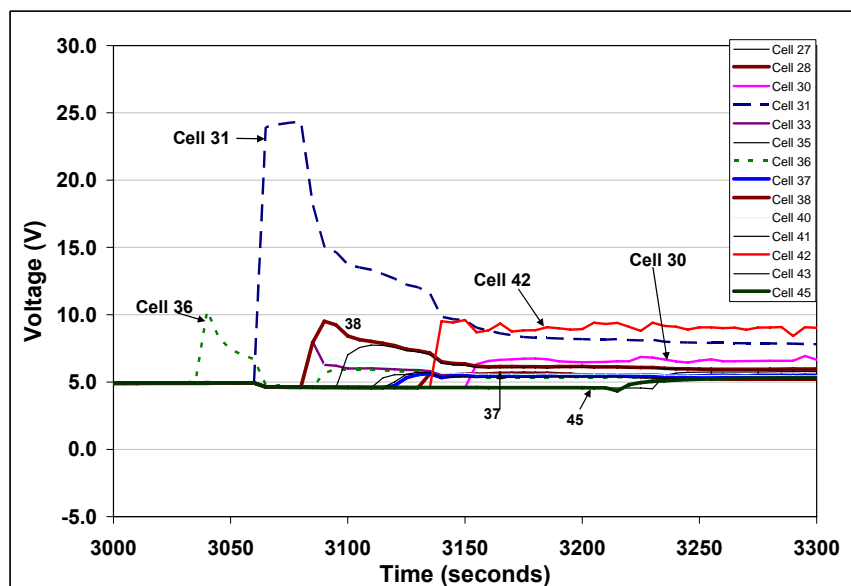


Figure 15. Expanded View of the First Half of the Overcharge Test on 14S set of cells using a current of 1.5 A

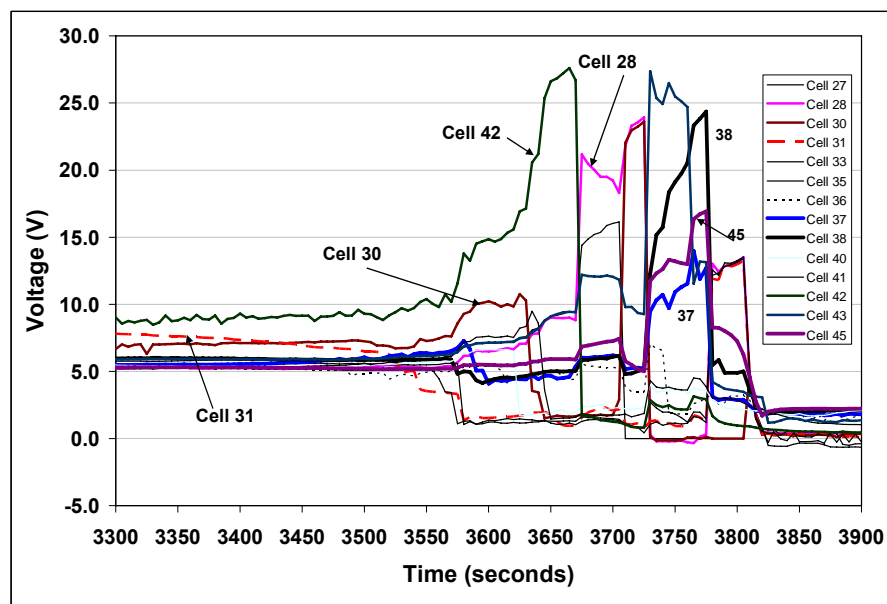



Figure 16. Expanded View of the Second Half of the Overcharge Test on 14S set of cells using a current of 1.5 A

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In conclusion, the internal protective devices such as the PTC and CID found in small cylindrical commercial Li-Ion cells do not provide the expected protection in high voltage and high capacity battery designs. If these are to be used as safety controls, their protection in the relevant string or bank configuration should be verified by test before used to design and build flight batteries.

Summary of Results:


The results of the tests on the series cell strings confirmed that the PTC had a voltage limitation and this value varied with cell manufacturer. Both the PTC and CID protect 100 % of the time in single cells but do not always protect in multi-cell strings and banks. In multi-cell banks, the reaction of the cells to an overcharge condition depended on the charge current and end-of-charge voltage. If the charge current was high enough to cause PTC activation of any cells in the bank and the cell/cells with activated or tripped PTCs were exposed to a high voltage setting on the power supply (as with the 48 V, 24 A, 16-cell bank), the results were catastrophic and protection by CID opening was not observed. The high-voltage setting on the power supply simulates a high voltage battery pack that the cell bank is a part of. Similarly, the CIDs do not protect if the cell bank had cells with their PTCs compromised or activated and the results were catastrophic again (as seen with those removed from the Canon battery pack). It was also observed that if the charge currents were high enough to cause unhindered cell heating (as with the 12 V, 24 A, 16-cell bank test), even after the charge was terminated, the cells go into a thermal runaway condition. In summary, both the PTC and the CID cannot be completely relied on for protection under external short and overcharge conditions respectively due to the limitations on these devices.

Recommendations:

To prevent battery modules from going into a catastrophic hazardous condition, the voltage seen by any one PTC in the event of an external short should not be higher than its withstanding voltage. Cells should not have their PTCs compromised during the lot testing, qualification or battery assembly process. The current used for charging should not be high enough to cause PTC activation in cells especially if they are in a high-voltage module. If PTCs and CIDs are used as a level of control, their safe activation should be confirmed by actual testing and reconfirmed on every new flight lot.

Acknowledgment:

Mobile Power Solutions is thanked for the help in carrying out all the parallel bank external short and overcharge tests. Applied Power International is thanked for carrying out all the series string external short and overcharge tests.

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Appendix K. Overview of diode scheme

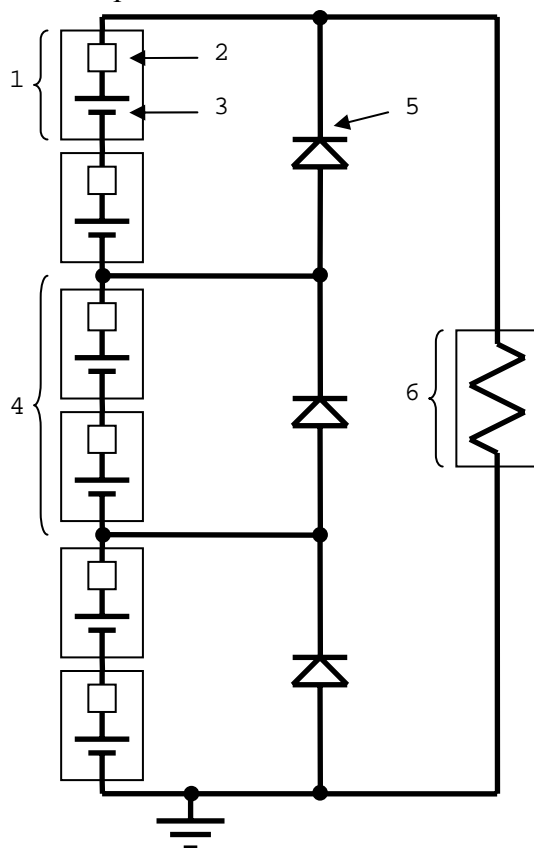
Frank Davies

There are failure modes of a series string of cells which can impose the full string voltage across components of the cells. If the impedance of a cell component in the string increases dramatically while the battery is driving a load, the cell component could experience high voltages if its impedance exceeds the load impedance. Commercial Lithium Ion cells often have a PTC current limiting device built into the cell. The PTCs in commercial cells are often not rated for more than 40 volts. If cells with such PTCs are used in a string with a total voltage greater than the PTC rating, the PTCs will fail if the string is shorted.

Diode scheme operational description

If diodes are placed in parallel with groups of cells as shown below, the maximum voltage that may appear across a PTC is limited to less than the total string voltage.

Reverse diodes across substrings help with other high impedance cell conditions (tripped CID, shutdown separator, discharged cell) by holding down the maximum voltage that can appear across the impedance.



1. Battery cell with built-in short circuit protection.
2. Internal short circuit protection device (PTC). May be similar to Raychem Polyswitch.
3. Electrochemical part of cell (provides electromotive force)
4. Substring
5. Diode
6. Load.

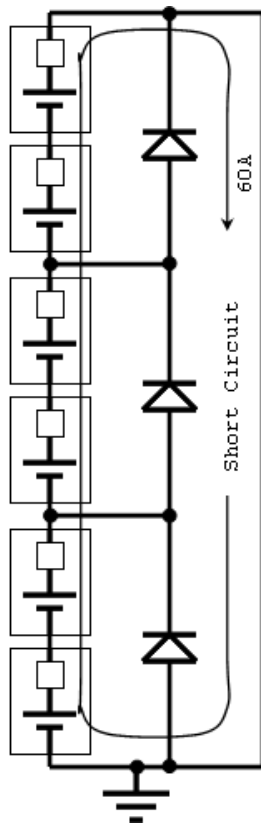
Notes:

- A. More than two battery cells per substring may be used.
- B. More than 3 substrings may be used.
- C. The example battery system presented here is of limited size and complexity for clarity.

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Trip sequence example: Stage 1

Short circuit appears. All PTC short circuit protection devices start heating up.



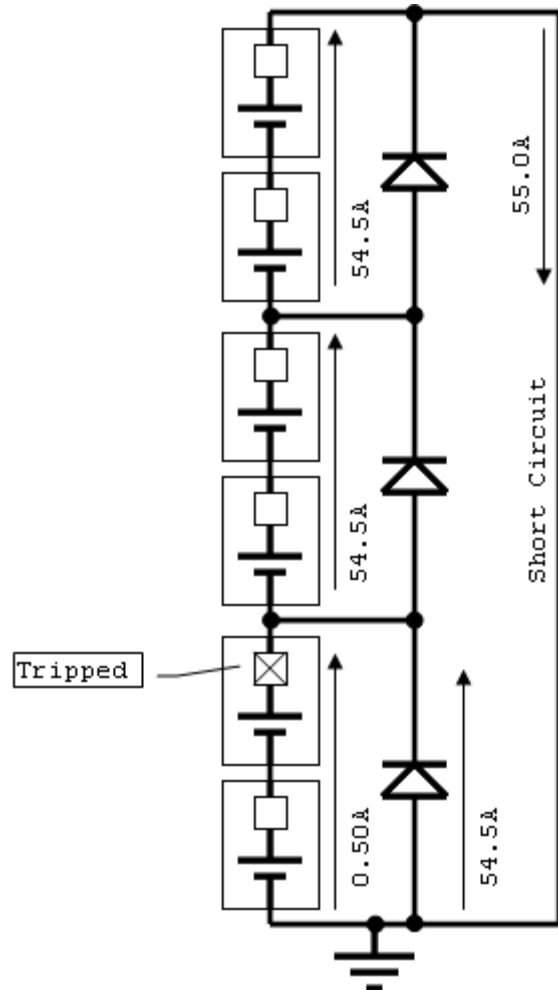
Notes:

1. No current through diodes yet.
2. Short circuit current is limited by cell impedances and cold PTC impedances.
3. This stage may last several seconds, depending on PTC characteristics.

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Trip sequence example: Stage 2

First PTC trips, shunting current through diode.



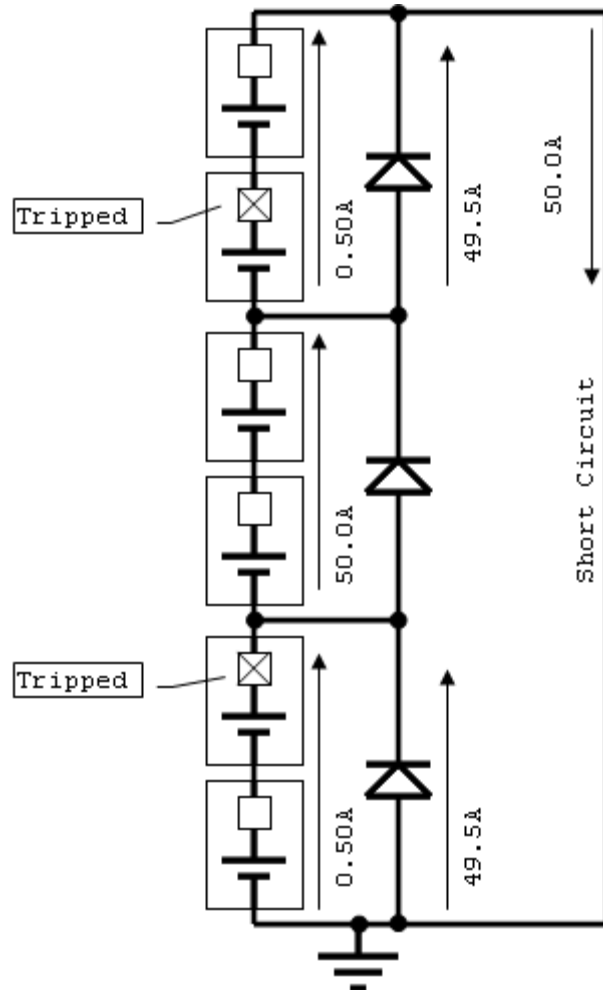
Note:

1. Small current flows through shorted substring, keeping PTC tripped.
2. Current through short is reduced, but not dramatically, since the current is still basically limited by the cell impedances. Other substrings have not tripped yet.
3. Maximum voltage across tripped PTC is two cells worth plus diode drop.
4. Diode takes almost maximum short circuit current until trip sequence is complete.
5. Which substring trips first depends on device tolerances.
6. This stage may last 0.1 seconds or so.

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Trip sequence example: Stage 3

Second PTC trips, shunting current through diode and reducing current



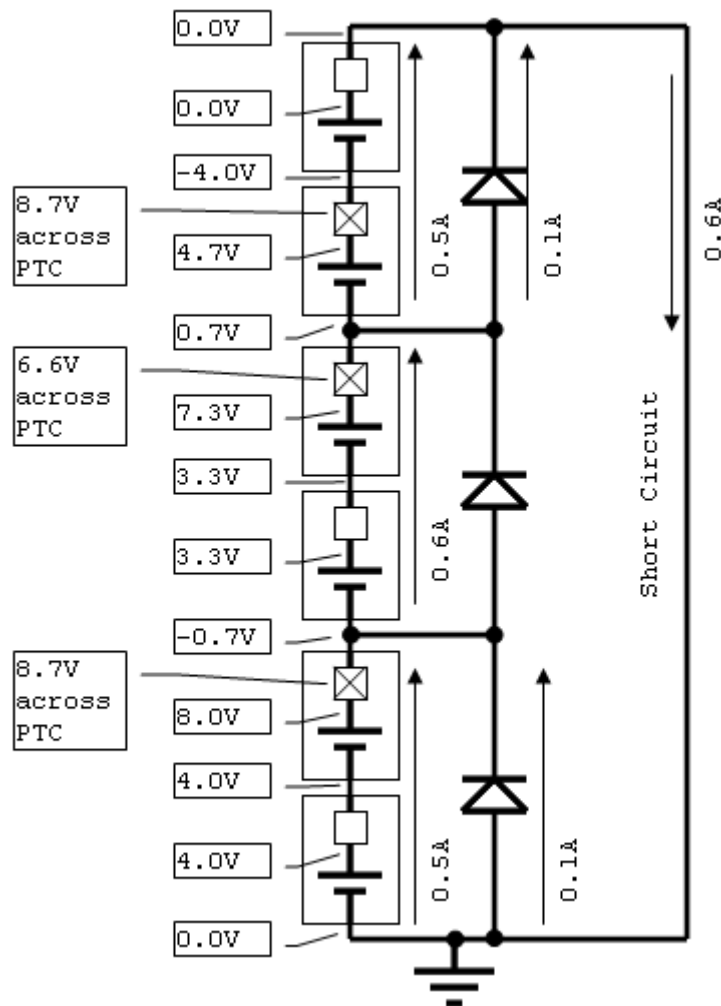
Note:

1. Small current flows through shorted substring, keeping PTC tripped.
2. Current through short is reduced again, but still high.
3. Maximum voltage across tripped PTC is two cells worth plus diode drop.
4. When one PTC in a substring trips, it inhibits the tripping of the other PTCs in that substring by reducing the substring current.
5. Which PTC in a substring trips first depends on device tolerances.
6. This stage may last 0.1 seconds or so.

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Trip sequence example: Stage 4

Last PTC trips, reducing current through short to low levels.



Notes:

1. Last diode does not get forward biased (conduct current).
2. Last substring to trip still runs low level current through the diodes of the other substrings and the short.
3. The tripped PTC device in the last substring to trip does not get quite as large a voltage across it as the other tripped PTCs.
4. If the short is removed, then no current will flow through the PTCs, and they will cool down, resetting themselves to a low impedance state.
5. High impedance shorts may result in one or more substrings not tripping. In any event, current will be limited to the PTC trip level or lower.
6. This stage lasts until the short circuit is removed (or the cells discharge).

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PTC Characteristics

1.1 Overview

Since the PTCs are an integral part of the cells, there is not much latitude for design decisions. However, the characteristics of the PTC selected by the cell manufacturer have a significant impact on battery system performance. Cell manufacturers may provide more detailed technical information if asked. Testing on cells and on PTCs removed from cells (ends of cell cases) may be necessary to obtain design data.

1.2 PTC impedance variations

PTC impedance changes considerably after the first trip. Subsequent trips do not cause much change.

For example, Doljack [1] states that the resistance of a PTC 1 hour after its first trip may be 20% higher than the initial (pre-trip) resistance. After 24 hours it may have decreased 5%.

1.3 Sustaining current


Under a persistent short, PTCs allow a leakage current to flow that keeps them at their transition temperature (the temperature at which the PTC changes rapidly with temperature). Test data shows that a typical 18650 Li ion cell PTC requires about 3W to sustain itself at the tripped temperature. If a substring has 4 cells in it (OCV= 4*3.6V average), then the sustaining current would be about $3W/14.4V = 208 \text{ mA}$.

1.4 Variation of performance.

Dependence of performance on ambient temperature, trip history, and part-to-part variation means that a large margin must be designed between the normal operating currents and the expected trip currents. For example, the Raychem SMD075 (a discrete PTC, not a cell component) is rated as follows:

Raychem SMD075				
	0°C	20°C	40°C	60°C
Hold current	0.84A	0.75A	0.62A	0.49A
Trip current	1.68A	1.50A	1.24A	0.98A

A battery application that used this PTC over a 0°C to 40°C temperature range would have a maximum operating current (hold current) of 0.62A and a minimum trip current of 1.68A. Wire connected protected by this PTC would have to be sized to handle 1.68A, more than 250% of the maximum load current.

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1.5 Peak power limitations.

The PTCs are present in the cell to limit the energy available from the cell during a short. As such they also limit the peak power from the cell, particularly with hot batteries. When driving a constant power type load, such as a motor controller, the PTCs may cause the battery voltage to collapse toward the end of the mission when the battery is hot, the voltage is dropping, and the current is rising. Because of the lack of definition of PTC parameters, this must be determined by test. A suitable test might be to run a scaled worst case mission current profile on a single cell in an appropriate thermal environment and monitor for PTC activation. The test could be repeated while increasing the current or temperature until trip occurred to determine the design margin.

1.6 Battery overheating

Under a persistent short, the PTCs allow a leakage current to flow that keeps them at their transition temperature (the temperature at which the PTC changes rapidly with temperature). They will hold this temperature and heat will flow into the rest of the battery until the electrical energy in the battery is exhausted. This may result in the battery temperature rising enough to cause thermal runaway. The diode scheme splits the available energy between several PTCs on the string, which will spread the heat but not reduce the total amount of thermal energy.

1.7 Cell seal failure

The PTC in a cell is a heater at one end of the cell positioned very close to the crimp seal. Under conditions of a persistent short the hot PTC can cause the crimp seal at the end of the cell to fail due to PTC heat generation. This failure mode has been observed in tests.

Diode selection

1.8 Reliability

A discussion of diode reliability is outside of the scope of this guide. The contract governing the design of the battery will have parts reliability guidelines. This section discusses the failure modes of the diode scheme, their effects, and possible design changes to mitigate them.

1.8.1 Failure mode: Diode short

The failed diode shorts the substring. If the battery has a single string (no parallel strings), then the overall battery voltage will drop by the substring voltage. One PTC in the substring will trip and limit the current magnitude after a short time (determined by test). The energy stored in the substring will eventually turn into heat in the tripped PTC. The thermal design of the battery assembly must be able to handle this without propagating the failure. If the string is in parallel with other strings, the string with the shorted cells may end up with overcharged cells. Placing multiple diodes in series will control the failure effects.

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1.8.2 Failure mode: Diode open.

The failed diode does not affect the performance of the battery unless there is an external short. In that case, a complex series of events takes place which result in one or more PTCs in the substring with the failed diode seeing excessive voltage and failing short. Depending on the order in which the PTCs trip, the current in the short will not drop to low levels. Placing multiple diodes in parallel will control the failure effects.

1.9 Forward current rating

1.9.1 Peak current


During normal battery operation, no forward current flows through the diodes. The diodes must be sized to handle the current pulse that flows when the battery is shorted.

In the event of a hard external short circuit on the battery assembly the initial short circuit current will be limited by the cell impedances. After a short time, the first PTC will trip. This will shunt the short circuit current through the diode in parallel with that substring as well as reduce the short circuit current slightly. The second PTC (in another substring) will then trip and shunt the short circuit current through its diode and reduce the short circuit current somewhat. As the short continues more PTCs trip and the current decreases in a ramp until each substring has a tripped PTC. At this point the short circuit current is equal to the PTC trip sustaining current.

The diode that sees high current first is the one associated with the first PTC to trip. It does not actually see current until that PTC trips. Since once the first PTC has tripped, the others are about to trip and the current is dropping. This means that the durations of the current seen by diodes depend on the spread in trip times of the PTCs.

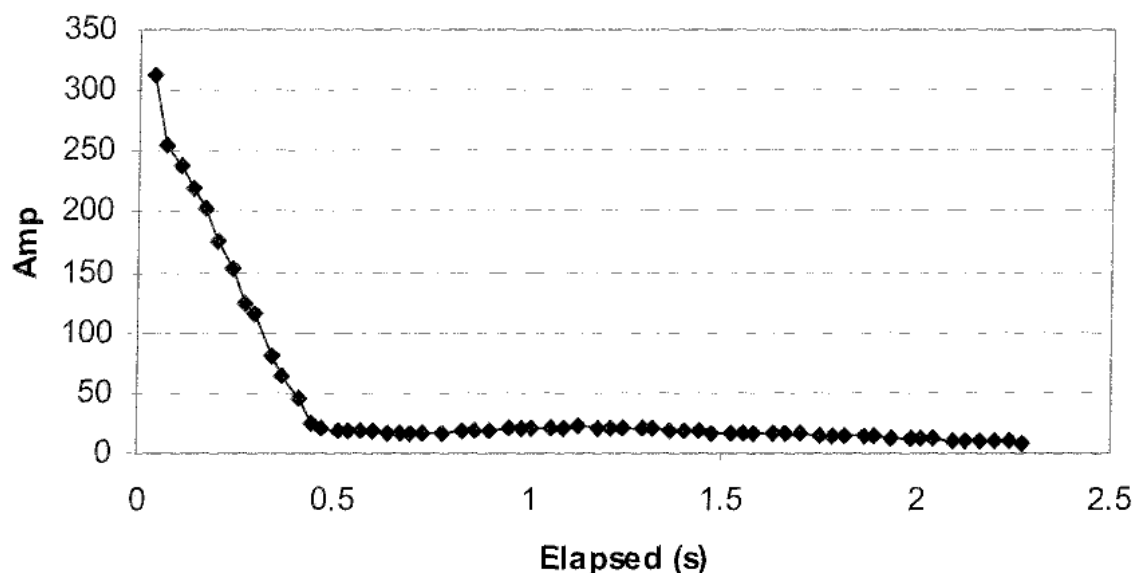
Because of these factors the exact current waveform that a diode will see can not be determined without a statistical model of PTC performance and detailed computer modeling, but it is possible to envelope it. The diode that sees the worst current will not see current higher than the hard short current of the cells (current limited by cell impedance and intercell connections). This can easily be determined by testing cells.

Estimating the duration of the diode current pulse is more difficult. For hard shorts, it is reasonable to use the PTC trip time of a cell under hard short. For lower magnitude shorts, a reasonable estimate of worst case diode current would be a rectangular pulse with a magnitude of 3 times the PTC room temperature “do not trip” current (as measured by test) and a duration of the trip time at that level.

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Standard diode data sheets do not generally have enough data to allow the diode to be well sized with this information. The best approach is to run these current waveforms on diodes with flight-like thermal environments and determine the maximum junction temperature.

Hard short test: 5P41S 18650 cells test string (5 strings in parallel)



1.9.2 Steady state current


A high resistance “smart” short could be of such a resistance that it would cause some but not all of the substrings to trip. This would mean that the diodes associated with the tripped substrings would carry high currents until the battery discharged. The diodes should be sized to carry the largest steady state current that the cells can supply without tripping PTCs.

1.10 Reverse blocking voltage

The diode must normally sustain the voltage of the fully charged substring. In the event of a cell in the substring having a jump in impedance during charge (CID opening, shutdown separator, or PTC activating), the diode may be called on to tolerate the maximum charger voltage minus the voltage of the other substrings.

1.11 Reverse leakage current

During normal operations, the reverse leakage current of the diode will act to discharge the substring. A diode should be chosen with a leakage current significantly less than the equivalent self discharge current of the cells. Variations of leakage current from diode to diode can lead to

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cell imbalance if the leakage current is a significant fraction of the self discharge. Leakage current will produce a small heating effect which should be considered. Since reverse current is strongly temperature sensitive, the leakage current at the maximum storage temperature of the battery must be considered. Diode with leakage current that rises quickly with temperature may enter thermal runaway in poor thermal environments (high temperature, vacuum, etc). For example, self-discharge of typical 18650 cell designs at 25°C and 40% state-of-charge is on the order of 1.5% per year [2]. If the cell capacity is 2.4Ah, that amount of capacity loss over a year equates to a 4 μ A leak. Therefore, acceptable diode leakage rates must be below this level to preclude the diodes from cause cell to cell capacity imbalances during storage.

Test outline

1.12 Overview

Because the design of the battery system and the diode scheme depend on poorly documented properties of the diodes (transient thermal performance) and PTCs (maximum voltage, self-heating rate, trip time, etc.), these properties must be determined by test.


Test outline:		
PTC tests:	Peak short circuit current	Use sufficient number of cells in series so that circuit resistance is less than one tenth of Re of cells. Do not use number of cells that will cause overvoltage damage. Condition cells with low current trip, then relaxation time >1 day. Run at ambient, worst case cold, and worst case hot. Measure current during trip. Hold short on cells for one hour. Verify nominal operation after test (charge/discharge cycle). Measure peak current, duration of current pulse
	Reverse voltage test on individual cells.	Use power supply or stack of cells (without PTC, may be another chemistry such as NiCd) in series with a single cell. Increase voltage of power supply or cell stack until PTC fails. Repeat with several cells to characterize reverse voltage capabilities of cell PTCs. Build cell string with final diode design and full voltage. Test with short circuit at worst case temperatures.
	PTC do not trip levels	Trip fresh cells at increasing levels to determine the highest current that discharges the cell before PTC trip. Perform at high and low temperatures.
	PTC thermal generation	Measure thermal power generated by tripped PTCs at different voltage levels. May be combined with other tests.
Diode tests:	Diode	Characterize diode forward voltage vs temperature with

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	junction temp test	small test current and externally imposed temperature.
	Leakage current	Characterize diode leakage current at proposed mission voltage and temperature conditions. Select only diodes whose maximum leakage current is lower than cell self-discharge rate at planned storage and mission conditions.
	Diode thermal performance test	Diode mounted as it will be in final design, at worst case hot, ambient, and worst case cold. Using programmable power supply, put worst case current waveform at that temperature into diode. Repeat with current waveforms interrupted by test current at different intervals to evaluate junction temperature.
System thermal test:	Thermal model validation test	Substring in relevant thermal environment. Hard short in worst case hot at full charge. Keep hard short on cells while monitoring temperatures of cells. Let test continue until temperatures start dropping. Repeat with fresh substring at smart short.

References

- [1] Frank A. Doljack , “PolySwitch PTC Devices – A New Low-Resistance Conductive Polymer-Based PTC Device for Overcurrent Protection” *IEEE Transactions On Components, Hybrids, And Manufacturing Technology*, vol CHMT-4, No.4, December 1981
- [2] Tim J. Nelson, “Moli 18650J Li-ion Cell Performance Testing, SRI Report #32H, November 2004.

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Appendix L. Effects of High Charge Rates of Li-Ion Cells

Problem Description, Proposed Solutions, and Risk Assessment

Problem description: Lithium-ion batteries operate over wide temperature range, typically -20 to $+40^{\circ}\text{C}$, unlike the aqueous battery systems. However, there are constraints on their charge rates, especially at low temperatures. Due to hindered kinetics for Li intercalation, lithium tends to reduce as metal on the graphite anode. Such plated lithium may reversibly oxidize during discharge, at a lower potential than graphite or higher cell voltage, manifesting as a (high) voltage plateau, about 100 mV higher than the expected discharge voltages, as shown in Fig. 1. Even though, the plated lithium is reversible or may chemically intercalate into graphite over time, its presence at the anode surface will mean an accelerated degradation of the electrolytes, reduced cycle life, reliability and may be even unsafe.

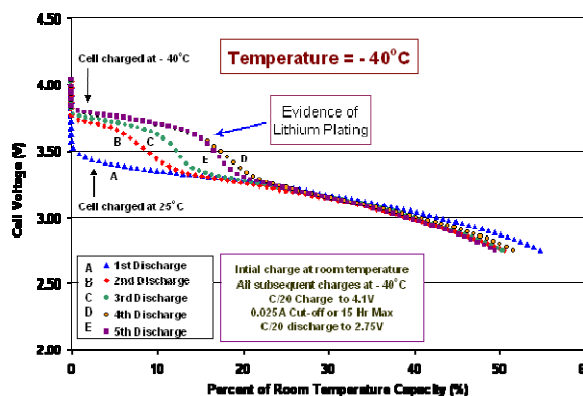



Fig. 1: Discharge curves of SAFT DD Li-ion cells at -40°C , following charge at -40°C . Curve represents a charge at room temperature

Proposed solution and Risk Assessment: A systematic study has been undertaken to determine conditions that ensure safe charging of Li-ion batteries under such extreme conditions of charge rate and temperature, specifically at low temperatures. The approach adopted here was to evaluate lithium-ion cells, with different electrolytes, electrode capacity ratios and configurations from different manufacturers for their ability to support such charge rates without any adverse effects, e. g., Li plating at low temperatures. In this process adequate screening methods were developed to identify the lithium plating phenomenon.

The test articles utilized in this study include: i) SAFT DD cells with a low temperature electrolyte (2007 pedigree, with 1.0M LiPF_6 in EC+EMC (20:80 v/v%)), ii) Yardney 7 Ah cells, with chemistry similar to the batteries on the Mars Exploration Rovers, iii) Quallion 18650 cells, iv) Quallion pouch cells of 4 Ah with three different electrolytes, v) SKC polymer cells, and vi) A123 26650 cells of 2.3 Ah. In addition, a few laboratory glass cells with carbon anodes and nickel cobalt oxide cathodes and Li reference electrodes were employed to understand the role of electrolytes on the plating characteristics. The cells were charged at different charge rates, up to C rate, at various temperatures down to -40°C , followed by discharge at the same temperatures but at constant current corresponding to C/10. The discharge profiles were examined to determine the on-set of Li plating in the preceding charge. In short the risk of lithium plating has been assessed in several likely prototype cells to identify the charge conditions not conducive to

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lithium plating and to establish the conditions permitting such Li plating and hence need to be avoided from the performance, reliability and safety standpoint.

Data Analysis

Lithium plating is a result of relatively slow kinetics for Li intercalation (into graphite) compared to Li deposition and is thus governed by all the conditions that affect the interfacial properties at the anode. More specifically, it is dependent on the: i) nature of electrolyte, ii) nature of anode composite electrode, and iii) cathode to anode capacity ratio. Generally, Li-ion cell designs are cathode limited. However, if anode is not sufficiently in excess, it may be polarized heavily during charge, which will drive the anode to potentials conducive to Li plating. Further, the cathode to anode ratio may change upon cycling/storage, due to a relatively faster degradation of the anode capacity. Our studies confirm these dependencies as shown below:

Effect of electrolyte: A low temperature electrolyte provides suitable interfacial conditions that would facilitate Li intercalation and hence would not pose the problem of Li plating. Fig.2 and 3 give example of two electrolytes: i) Ethylene carbonate-rich formulation (in Fig. 2), and ii) a low EC-content blended electrolyte, good for low temperature operations.

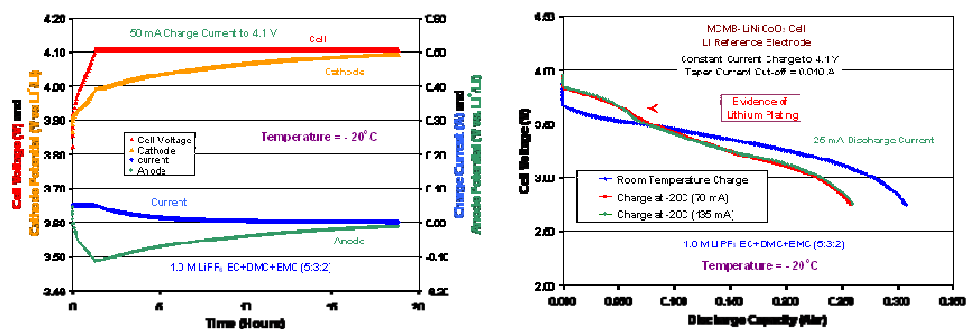



Fig. 2 Cathode and anode potentials during charge at -20°C and cell discharge curves during subsequent discharge, showing Li plating in high EC electrolyte

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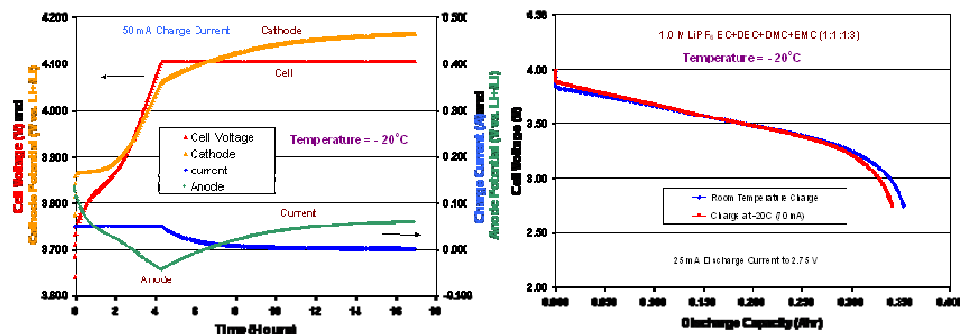


Fig. 3: Cathode and anode potentials during charge at -20°C and cell discharge curves during subsequent discharge, showing no evidence of Li plating in one of JPL's low temperature electrolytes

As may be seen from the above figures, the low temperature electrolyte provides suitable interface for (good) Li intercalation kinetics and less so for Li plating. This is further substantiated by the Tafel polarization data, which show the relative kinetics at the individual electrodes, as shown in Fig. 4.

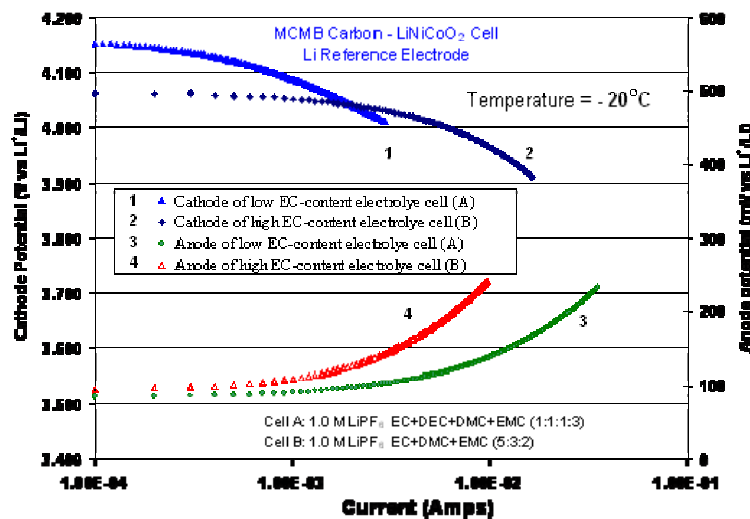



Fig. 4: Tafel polarization curves of cathodes and anodes at -20°C in contact with the EC-rich and low-EC (low temperature) electrolytes.

It is clear from the above figure that the anode kinetics are slower compared to the cathode kinetics in the EC-rich electrolyte, which would have subjected the anode to a heavier polarization and subsequently to lithium plating, as observed (cf. Fig. 2).

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Effect of anode to cathode ratio: High anode to cathode (capacities) ratio will minimize polarization at the anode during charge, which in turn precludes Li plating on the anode. Figs 5 and 6 provide a comparison of the two prototypes, which differ more prominently in the anode to cathode ratio among other design variations.

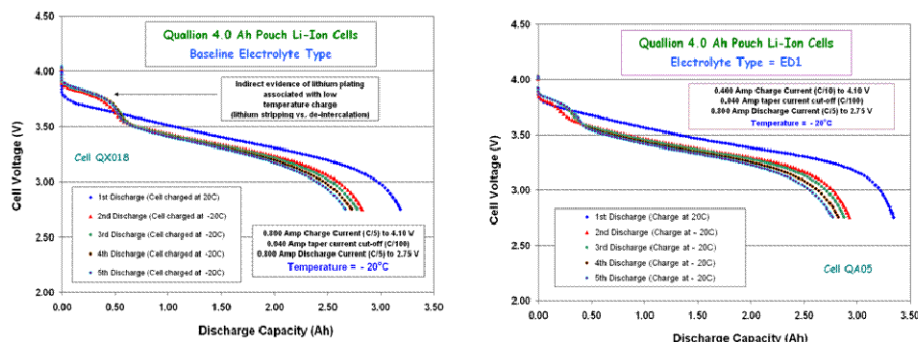


Fig. 5: Charging of Quallion pouch cells, with the baseline and a low temperature electrolyte, at -20°C and subsequent discharge cell discharge curves showing strong tendency of Li plating.

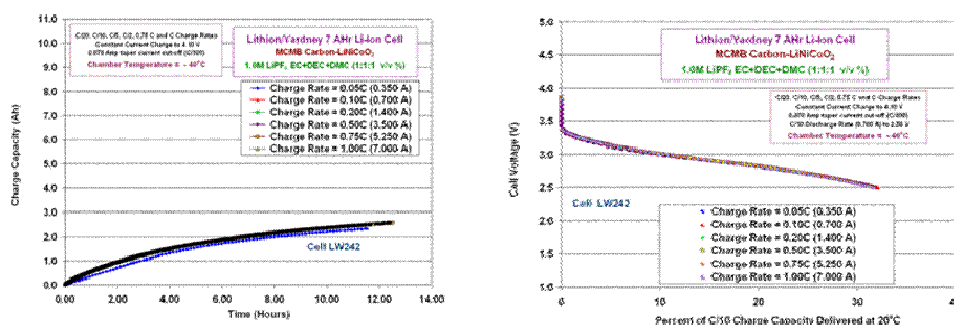


Fig. 6: Charging of Yardney 7 Ah cells with JPL's gen-1 low temperature electrolytes at different charge rates at -40°C and subsequent discharge curves showing no evidence of Li plating.

The cells shown in Fig. 5 were fabricated by Quallion in pouch configuration and have capacities of 4 Ah. Based on their specific energies of about 190 Wh/kg (and also our personal discussions), we conclude that these cells have a lower anode to cathode ratios. This may be a significant factor behind the tendency towards lithium plating at -20°C, with baseline as well as with low temperature electrolytes. The cells shown in Fig. 6, made by Yardney, on the other hand have higher anode to cathode ratio inferred from their modest specific energies and are immune to lithium plating even at -40°C.

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Intercalation vs. Plating Kinetics

To express the effect of kinetics rather quantitatively, we estimated the currents going towards Li plating and Li intercalation at a given potential. These estimates were made with the assumption that both Li processes are in the Tafel mode at the selected voltages. The value of reversible potential for Li intercalation used for this calculation is 85 mV vs Li, while the potential for Li plating: 0 V vs. Li. As may be seen from the figure, proportion of plating current starts climbing up from ~ 2% to > 10%, if the ratio of exchange currents for intercalation to plating goes below 20. In other words, if the intercalation kinetics are only 20 times faster than plating (which is the case at low temperatures), lithium plating current starts being substantial.

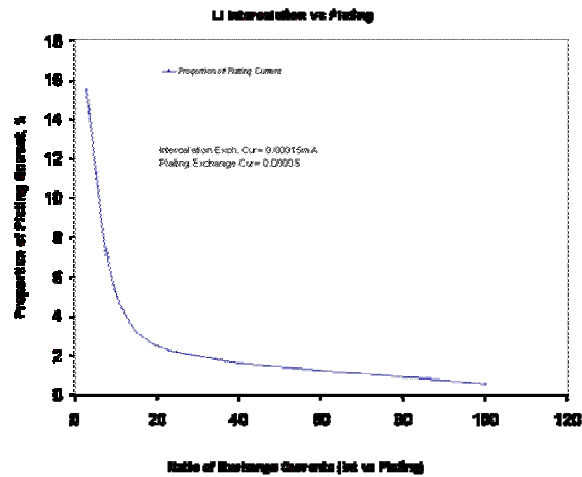



Fig. 7: proportion of plating current as a function of the relative kinetics for plating and intercalation

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Summary of the Test Data

Table-1 summarizes the findings from different prototype cells tested in this program. It lists the charge rates (in terms of C rate) of these different cells, that are acceptable (without Li plating) at different temperatures.


Table -1: Demonstrated Li plating as a function of charge rate and temperature

Temperature	Charge rate	Yardney	A123 (COTS)	Quallion baseline (18650-	Quallion-ED1	Quallion-ED2	SKC	SAFT (EC+EMC)
	Charge Voltage	4.1 V	3.6 V	4.2	4.1	4.1	4.2	4.1
0	C/10	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating
	C/5	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating
	C/2	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating
	C	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating	No Plating
-10	C/10	No Plating	No Plating	No Plating	No Plating	NA	No Plating	No Plating
	C/5	No Plating	No Plating	No Plating	No Plating	NA	No Plating	No Plating
	C/2	No Plating	No Plating	No Plating	No Plating	NA	No Plating	No Plating
	C	No Plating	Possibly	No Plating	No Plating	NA	No Plating	No Plating
-20	C/10	No Plating	No Plating	No Plating	Plating	Mild	Mild	No Plating
	C/5	No Plating	No Plating	No Plating	Plating	Plating	Mild	No Plating
	C/2	No Plating	Plating	Plating	Mild	Plating	Mild	Mild
	C	No Plating	Plating	Plating	Low capacity	Mild	Mild	Mild
-30	C/10	No Plating	Possibly	Plating	Low capacity	NA	Mild	Plating
	C/5	No Plating	Plating	Plating	Low capacity	NA	Mild	Plating
	C/2	No Plating	Plating	Plating	Low capacity	NA	Mild	Plating
	C	No Plating	Plating	Plating	Low capacity	NA	Mild	Plating
-40	C/10	No Plating	Low capacity	Negligible Ah	Negligible Ah	Negligible Ah	Possibly	Low capacity
	C/5	No Plating	Low capacity	Negligible Ah	Negligible Ah	Negligible Ah	Possibly	Low capacity
	C/2	No Plating	Low capacity	Negligible Ah	Negligible Ah	Negligible Ah	Possibly	Low capacity
	C	No Plating	Low capacity	Negligible Ah	Negligible Ah	Negligible Ah	Possibly	Low capacity

As may be seen from the above table, the propensity for Li plating as a function of charge rate and temperature varies significantly from one manufacturer to another. These variations may be related to the difference in materials, electrode and electrolytes, and in the cell designs, more importantly the amount of anode reserve.

Yardney 7 Ah Cells

As mentioned previously, a number of 7 Ah Li-ion manufactured by Yardney Technical Products were subjected to charge characterization testing at a number of temperatures (i.e., 20, 10, 0, -10, -20, -30, and -40°C) and using a number of charge rates (C/20, C/10, C/5, C/2, C/1.33, C/1.0). As shown in Table 1, when the cells were evaluated at 20°C, comparable capacity can be obtained in all cases, regardless of charge rate. This is due to the charging methodology consisting of implementing a constant current-constant potential (CC-CV) protocol, which allows the current to taper to a fixed value (i.e., C/50, or 0.140A) in the constant potential mode (e.g., 4.10V). Although the final charge capacity is comparable regardless of charge rate, proportionately more charge time is spent in the constant potential mode when high inrush charge currents are used, and lower watt-hour efficiencies are observed due to increased polarization. These differences are illustrated in Figs. 8 and 9, in which the charge

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characteristics are displayed for one of the cells at 20°C using C/5 and C charge rates, respectively. As shown in Fig. 8, when a C/5 charge rate is used the cell is in the constant current mode for 5.48 hours of the total 6.54 hour charge time, or ~ 85% of the total charge time. In addition, 7.697 Ah is charge capacity is accepted by the cell in the constant current mode, representing 95.6% of the total charge capacity.

Table 2: Summary of the charge characteristics of a Yardney 7 Ah cell at 20°C.

			Cell LW 242 1.0 M LiPF ₆ EC+DEC+DMC (1:1:1 v/v %)						
Temperature	Charge Rate	Discharge Current (A)	Charge Capacity (Ah)	Charge Time (Hours)	Percent C/10 Capacity	Percent C/10 Capacity at 20°C	Charge Watt-Hr (Wh)	Discharge Watt-Hr (Wh)	Watt Hour Efficiency (%)
20°C	0.05C	0.350	8.0568	23.3474	100.00	100.00	29.5035	28.9212	98.03
	0.10C	0.700	8.0523	12.0724	99.94	99.94	29.5767	28.9385	97.84
	0.20C	1.400	8.0533	6.5373	99.96	99.96	29.7489	28.9385	97.28
	0.50C	3.500	8.0492	3.3486	99.91	99.91	30.1778	28.9183	95.83
	0.75C	5.250	8.0396	2.6752	99.79	99.79	30.4619	28.8823	94.81
	1.00C	7.000	8.0324	2.4127	99.70	99.70	30.7237		

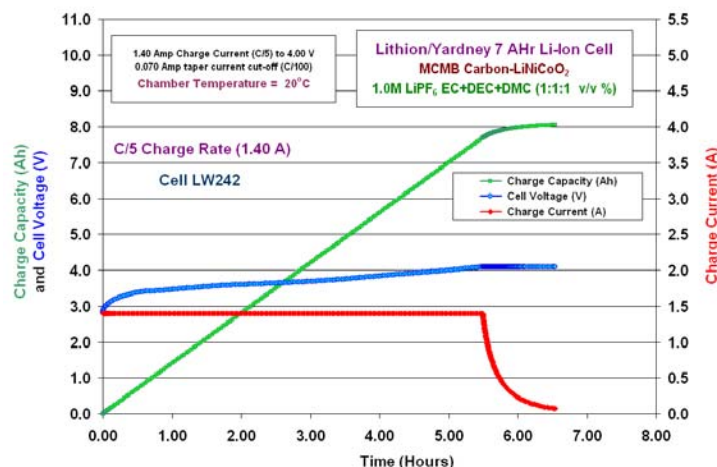



Fig. 8: Charge characteristics of a Yardney 7 Ah cell at 20°C using a C/5 rate to 4.10V

In contrast, when using a C rate charge, the cell is in the constant current mode for 0.95 hours of the total 2.41 hour charge time, or ~ 39% of the total charge time. In addition, 7.697 Ah is charge capacity is accepted by the cell in the constant current mode, representing only 82.6% of the total charge capacity. Generally speaking, due to decreased cell resistance, high power cell designs typically have improved charge acceptance characteristics at high rates, and proportionately more charge capacity is obtained in the constant current mode as opposed to the

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constant potential mode. In contrast, cells with poor rate capability and/or cells that have impedance growth due to aging effects will typically have a larger proportion of the charge capacity being accepted during the constant potential mode.

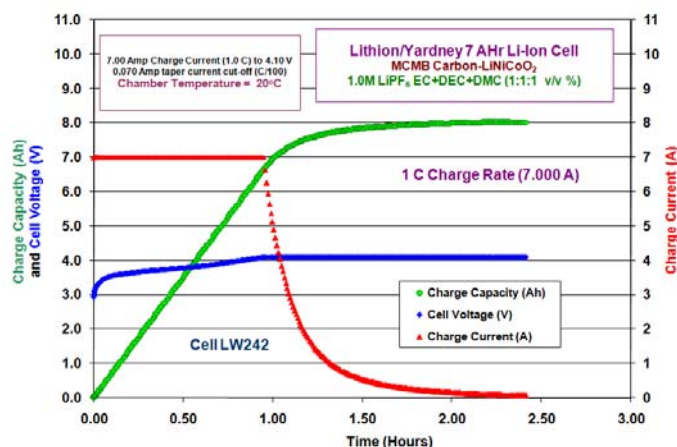


Fig. 9: Charge characteristics of a Yardney 7 Ah cell at 20°C using a 1.0 C rate to 4.10V

This trend is also seen at lower temperatures, where more of the charge capacity is accepted during the constant potential mode rather than in the constant current mode, due to higher cell resistance. This results in correspondingly higher charge times to obtain “full” capacity. It should also be noted that lower charge capacities are obtained at lower temperatures, resulting in ~ 96 %, 90%, 83%, 75%, 61%, and 32% of the room temperature capacity being charged at 10°, 0°, -10°, -20°, -30°, and -40°, respectively. For example, when a cell was characterized at -20oC, as summarized in Table 2, only 74-75% of the room temperature capacity could be charge into the cell, regardless of charge rate employed. In addition, the charge times required to charge the cell is much longer, with the C rate charged taking over 7 hours to reach full capacity. This is illustrated in Fig. 10, in which the charge characteristics of a 7 Ah cell are shown at -20oC using a C rate charge. As shown, only negligible charge capacity is accepted by the cell during the constant current mode, the cell being unable to support such high charge currents at these temperatures without being polarized above the set charge voltage of 4.10V. Thus, nearly all of the capacity is obtained during the constant potential mode, with over half of the capacity being accepted when the current has taper to values below 3A.

Table 2: Summary of the charge characteristics of a Yardney 7 Ah cell at - 20°C.

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			Cell LW 242 1.0 M LiPF ₆ EC+DEC+DMC (1:1:1 v/v %)						
Temperature	Charge Rate	Discharge Current (A)	Charge Capacity (Ah)	Charge Time (Hours)	Percent C/10 Capacity	Percent C/10 Capacity at 20°C	Charge Watt-Hr (Wh)	Discharge Watt-Hr (Wh)	Watt Hour Efficiency (%)
- 20°C	0.05C	0.350	6.0073	19.2501	100.00	74.56	22.9359	20.5176	89.46
	0.10C	0.700	6.0227	11.8156	100.26	74.75	23.3408	20.6344	88.40
	0.20C	1.400	6.0162	8.5451	100.15	74.67	23.7861	20.6448	86.79
	0.50C	3.500	6.0065	7.2249	99.99	74.55	24.4212	20.5940	84.33
	0.75C	5.250	5.9762	7.1198	99.48	74.18	24.4775	20.4916	83.72
	1.00C	7.000	5.9380	7.1191	98.85	73.70	24.3436	20.3758	83.70

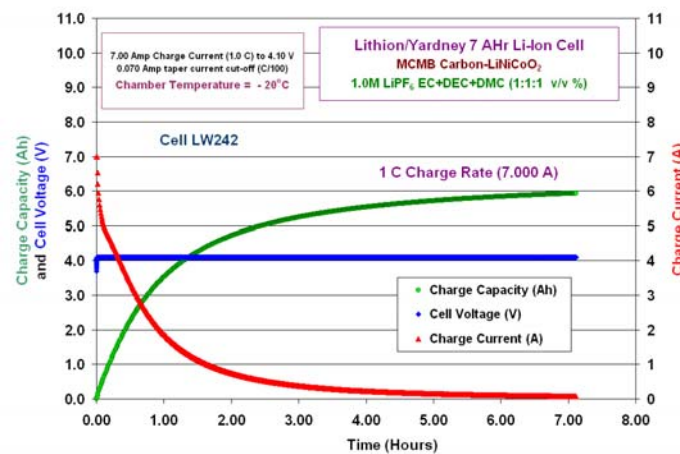



Fig. 10: Charge characteristics of a Yardney 7 Ah cell at -20°C using a 1.0 C rate to 4.10V

In terms of harmful lithium plating processes, the conditions that possess the greatest propensity for this occurring is when the charge current and the charge potential are the highest. Thus, in the case of the cell above under the described conditions (C rate charge at -20°C), the likelihood of lithium plating is greatest at the very beginning of the charging process, i.e., when the charge current is the highest (e.g. above 3.0A) and the charge voltage is the highest (e.g., 4.10V). When the subsequent discharge profiles are observed following high rate charge at -20°C, as shown in Fig. 11, no clear evidence of the corresponding lithium stripping phenomena is observed, indirectly suggesting that no significant lithium plating occurred or that any lithium that was plated at the higher currents intercalated into the graphitic anode over time when the cell was charging at the lower currents. For that matter, no evidence of lithium plating was observed (as ascertained by the subsequent discharge profiles) with the Yardney 7 Ah cells when characterized down to -40oC, and using charge rates of up to C rate. The summary of all the characterization tests performed on the baseline cell, which contained the ternary carbonate electrolyte (e.g., 1.0M LiPF₆ in EC+DEC+DMC (1:1:1 v/v %), is shown in Table. 2.

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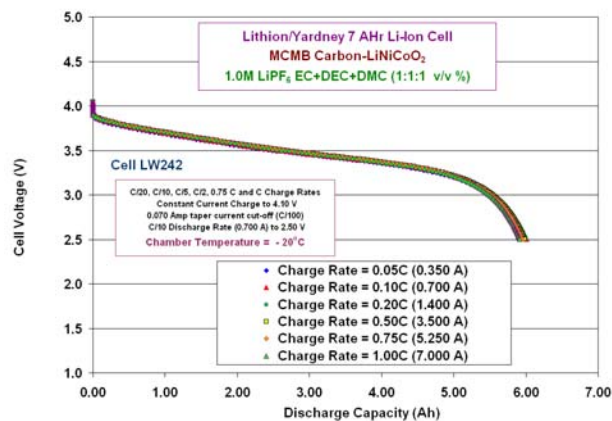



Fig. 10: Discharge profiles of a 7 Ah cell after charging at various rates at low temperature (- 20°C).

Table 2: Summary of the charge characteristics of a Yardney 7 Ah cell, containing the baseline electrolyte 1.0M LiPF₆ in EC+DEC+DMC (1:1:1 v/v %) at various temperatures .

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			Cell LW 242 1.0 M LiPF6 EC+DEC+DMC (1:1:1 v/v %)						
Temperature	Charge Rate	Discharge Current (A)	Charge Capacity (Ah)	Charge Time (Hours)	Percent C/10 Capacity	Percent C/10 Capacity at 20°C	Charge Watt-Hr (Wh)	Discharge Watt-Hr (Wh)	Watt Hour Efficiency (%)
20°C	0.05C	0.350	8.0568	23.3474	100.00	100.00	29.5035	28.9212	98.03
	0.10C	0.700	8.0523	12.0724	99.94	99.94	29.5767	28.9385	97.84
	0.20C	1.400	8.0533	6.5373	99.96	99.96	29.7489	28.9385	97.28
	0.50C	3.500	8.0492	3.3486	99.91	99.91	30.1778	28.9183	95.83
	0.75C	5.250	8.0396	2.6752	99.79	99.79	30.4619	28.8823	94.81
	1.00C	7.000	8.0324	2.4127	99.70	99.70	30.7237		
10°C	0.05C	0.350	7.7452	22.6225	100.00	96.13	28.5363	27.8336	97.54
	0.10C	0.700	7.7571	11.8935	100.15	96.28	28.7010	27.8456	97.02
	0.20C	1.400	7.7581	6.6386	100.17	96.29	28.9214	27.8356	96.25
	0.50C	3.500	7.7340	3.6653	99.86	95.99	29.3697	27.7578	94.51
	0.75C	5.250	7.7277	3.0941	99.77	95.92	29.7269	27.7027	93.19
	1.00C	7.000	7.7228	2.9136	99.71	95.85	30.0284		
0°C	0.05C	0.350	7.2584	21.4949	100.00	90.09	26.9728	25.9934	96.37
	0.10C	0.700	7.2665	11.5890	100.11	90.19	27.1700	26.0100	95.73
	0.20C	1.400	7.2649	6.8085	100.09	90.17	27.4519	25.9692	94.60
	0.50C	3.500	7.2390	4.2259	99.73	89.85	28.0234	25.8735	92.33
	0.75C	5.250	7.2338	3.8083	99.66	89.78	28.4049	25.8399	90.97
	1.00C	7.000	7.2195	3.6276	99.46	89.61	28.6730		
-10°C	0.05C	0.350	6.7039	20.3658	100.00	83.21	25.1701	23.7137	94.21
	0.10C	0.700	6.7180	11.5154	100.21	83.38	25.4718	23.7535	93.25
	0.20C	1.400	6.7108	7.3188	100.10	83.29	25.8389	23.7115	91.77
	0.50C	3.500	6.6941	5.2590	99.85	83.09	26.5356	23.6379	89.08
	0.75C	5.250	6.6737	4.9619	99.55	82.83	26.8405	23.5484	87.73
	1.00C	7.000	6.6562	4.9253	99.29	82.62	27.0337		
-20°C	0.05C	0.350	6.0073	19.2501	100.00	74.56	22.9359	20.5176	89.46
	0.10C	0.700	6.0227	11.8156	100.26	74.75	23.3408	20.6344	88.40
	0.20C	1.400	6.0162	8.5451	100.15	74.67	23.7861	20.6448	86.79
	0.50C	3.500	6.0065	7.2249	99.99	74.55	24.4212	20.5940	84.33
	0.75C	5.250	5.9762	7.1198	99.48	74.18	24.4775	20.4916	83.72
	1.00C	7.000	5.9380	7.1191	98.85	73.70	24.3436	20.3758	83.70
-30°C	0.05C	0.350	4.8979	17.5462	100.00	60.79	19.2008	15.7285	81.92
	0.10C	0.700	4.9060	12.5917	100.17	60.89	19.6208	15.8273	80.67
	0.20C	1.400	4.8917	11.0017	99.87	60.71	19.9209	15.7832	79.23
	0.50C	3.500	4.8458	10.9032	98.94	60.15	19.8666	15.6073	78.56
	0.75C	5.250	4.7908	10.9447	97.81	59.46	19.6417	15.4358	78.59
	1.00C	7.000	4.7384	10.9658	96.74	58.81	19.4268	15.2829	78.67
-40°C	0.05C	0.350	2.3155	11.5376	100.00	28.74	9.4238	7.4320	78.86
	0.10C	0.700	2.5426	12.1132	109.80	31.56	10.4195	7.4810	71.80
	0.20C	1.400	2.5536	12.4072	110.28	31.70	10.4692	7.4183	70.86
	0.50C	3.500	2.5583	12.4359	110.48	31.75	10.4887	7.4318	70.86
	0.75C	5.250	2.5640	12.5156	110.73	31.82	10.5120	7.4359	70.74
	1.00C	7.000	2.5637	12.5045	110.72	31.82	10.5108	7.4364	70.75

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Findings, Observations, and Recommendations

Li-ion cells upon charge at high rates and/or low temperatures can exhibit a tendency to have metallic lithium deposited on the carbon anode – a deviation from the intercalation process that the Li-ion chemistry was designed to accomplish (in contrast to Li metal systems). Such Li plating will have deleterious impact on the performance, reliability and maybe even safety. This characteristic is dictated by several parameters including the nature of electrode and electrolyte materials and the cell design parameters, especially the relative electrode capacities.

It is recommended that Li-ion cells and batteries be tested in the expected charge regime and temperature range before hand, before putting them for use. As a diagnostics, the cells may be charged at the relevant charge rate and temperature and one may look for the evidence for Li plating in a subsequent discharge, which will be in the form of a voltage plateau about 100 mV higher than normal in the early stages of discharge. It is recommended that some margin is allowed in the charge rates, since the relative electrode capacity ratios may get worse upon cycling, due to a relative faster degradation from the anode.

The plated lithium may partly be intercalated, either during the tapered charge mode or in the open-circuit stand, which we need to study further. Likewise, the long-term impact of such Li plating, though known to be harmful, needs to be understood.